

SUPERFUND TREATABILITY CLEARINGHOUSE

Document Reference:

Alliance Technologies Corp. "Technical Resource Document: Treatment Technologies for Dioxin-Containing Wastes." Technical Report EPA/600/2-86/096. 244 pp. October 1986.

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SUPERFUND TREATABILITY CLEARINGHOUSE ABSTRACT

Treatment Process: Thermal Treatment - Circulating Bed Combustion

Media: Soil/Generic

Document Reference: Alliance Technologies Corp. "Technical Resource Document: Treatment Technologies for Dioxin/Containing Wastes." Technical Report EPA/600/2-86/096. 244 pp. October 1986.

Document Type: EPA ORD Report

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Site Name: Denny Farm Site, MO (Non-NPL)

Location of Test: Denny Farm, MO

BACKGROUND: GA Technologies conducted the circulating bed combustor (CBC) pilot scale tests using PCB-contaminated soils. This treatability study compiles available information on those technologies for dioxin containing solids, liquids and sludges, many of which are in early stages of development. Discussion of the CBC pilot test is contained in this abstract. Other technologies in this document are discussed in Document Numbers FCFR-4 and FCFR-6. Technologies evaluated were those that destroy or change the form of dioxin to render it less toxic. Those technologies not tested on dioxin-containing wastes had been tested on PCB-containing wastes. The report divides the technologies into thermal and non-thermal groups for discussion. It was noted that incineration was the only sufficiently demonstrated technology for treatment of dioxin containing wastes (51 FR 1733) and RCRA Performance Standards for Thermal Treatment require 99.9999 percent destruction removal efficiency (DRE) of the principal organic hazardous constituent (POHC). Factors which affect the selection/use of a particular technology are discussed. Technical performance for treating a specific waste type and costs are both considered in this discussion. A summary of dioxin treatment processes, their performance/destruction achieved, and estimated costs are provided in Table 1. QA/QC is not discussed.

OPERATIONAL INFORMATION: GA Technologies conducted trial burns on PCB-contaminated soil with 9800 to 12,000 ppm of PCB. Auxiliary fuel was used to maintain the bed temperature at 1600° to 1800°F. A soil feed rate of 325 to 410 pounds per hour was used.

PERFORMANCE: A destruction efficiency exceeding six nines (99.9999 percent) was achieved. Costs of fluidized bed treatment are dependent on fuel requirements, scale and site conditions. Cost estimates of from \$27/ton to \$150/ton are provided for various assumptions.

CONTAMINANTS:

Analytical data is provided in the treatability study report. The breakdown of the contaminants by treatability group is:

<u>Treatability Group</u>	<u>CAS Number</u>	<u>Contaminants</u>
W02-Dioxins/Furans/PCBs	1336-36-3	Total PCBs

Note: This is a partial listing of data. Refer to the document for more information.

TABLE 1**SUMMARY OF DIOXIN TREATMENT PROCESSES**

<u>Process Name</u>	<u>Performance/Destruction Achieved</u>	<u>Cost</u>
Stationary Rotary Kiln Incineration	Greater than 99.999 DRE demonstrated on dioxin at combustion research facility	\$0.25 - \$0.70/lb for PCB solids
Mobile Rotary Kiln Incineration	Greater than 99.9999 DRE for dioxin by EPA unit; process residuals delisted	NA
Liquid Injection Incineration	Ocean incinerators only demonstrated 99.9 on dioxin-containing herbicide orange	\$200 - \$500/ton
Fluidized-bed Incineration	Greater than 99.9999 DRE demonstrated on PCBs	\$60 - \$320/ton
Infrared Incinerator (Shirco)	Greater than 99.9999 DRE on TCDD-contaminated soil	\$200 - \$1,200 per ton
High Temperature Fluid Wall (Huber AER)	Greater than 99.999 DRE on TCDD-contaminated soil	\$300 - \$600/ton
Molten Salt (Rockwell Unit)	Up to eleven nines DRE on hexachlorobenzene	NA
Supercritical Water Oxidation	99.9999 DRE on dioxin-containing waste reported by developer	\$0.32 - \$2.00/gallon
Plasma Arc Pyrolysis	Greater than 99.9999 destruction of PCBs and CCl_4	\$300 - \$1,400/ton
In-Situ Vitrification	Greater than 99.9% destruction on PCB-contaminated soil	\$120 - \$250/M ³
Solvent Extraction	Still bottom extraction: 340 ppm TCDD reduced to 0.2 ppm; 60-90% removal from soils.	NA
Stabilization/Fixation	Tests using cement decreased leaching of TCDD	NA
UV Photolysis	Greater than 98.7% reduction of TCDD	\$250 - \$1,200/ton
Chemical Dechlorination APEG processes	Reduction of 2,000 ppb TCDD to below 1 ppb for slurry (batch process)	\$296/ton for in situ, \$ 91/ton for slurry
Biological in situ addition of microbes	50-60% metabolism of 2,3,7,8-TCDD using white rot fungus	NA
Degradation using Ruthenium Tetroxide	Reduction of 70 ppb TCDD to below 10 ppb in 1 hr	NA
Degradation using Chloroiodides	Up to 92% degradation on solution of TCDD in benzene	NA

NOTE: Quality assurance of data may not be appropriate for all uses.

SUPERFUND TREATABILITY CLEARINGHOUSE ABSTRACT

Treatment Process: Thermal Treatment - Pyrolysis

Media: Soil/Generic

Document Reference: Alliance Technologies Corp. "Technical Resource Document: Treatment Technologies for Dioxin-Containing Wastes." Technical Report EPA/600/2-86/096. 244 pp. October 1986.

Document Type: EPA ORD Report

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Site Name: Times Beach, MO (NPL)

Location of Test: Times Beach, MO

BACKGROUND: This report focuses on the pilot scale Advanced Electric Reactor (AER). This treatability study compiles available information on those technologies for dioxin containing solids, liquids and sludges, many of which are in early stages of development. A discussion of the AER pilot test is contained in this abstract. Other technologies in this document are discussed in Document Numbers FCFR-3 and FCFR-6. Technologies evaluated were those that destroy or change the form of dioxin to render it less toxic. Those technologies not tested on dioxin-containing wastes had been tested on PCB-containing wastes. The report divides the technologies into thermal and non-thermal groups for discussion. It was noted that incineration was the only sufficiently demonstrated technology for treatment of dioxin containing wastes (51 FR 1733) and RCRA Performance Standards for Thermal Treatment require 99.9999 percent destruction removal efficiency (DRE) of the principal organic hazardous constituent (POHC). Factors which affect the selection/use of a particular technology are discussed. Technical performance for treating a specific waste type and costs are both considered in this discussion. A summary of dioxin treatment processes, their performance/destruction achieved, and estimated costs are provided in Table 1. QA/QC is not discussed.

OPERATIONAL INFORMATION: The AER, owned and operated by J.M. Huber Corporation, was used to treat, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). It was also used in other tests including tests at Gulfport, Mississippi, but these tests reported only removal efficiencies. Only two data points are present from the Times Beach trials, one from the treated soil and one from the baghouse catch.

The AER was operated at 3500°F-4000°F. Heating was accomplished using electrically heated carbon electrodes. A nitrogen purge gas provided the

reaction atmosphere. Since oxygen was not present, it was run in a pyrolytic manner.

PERFORMANCE: High DREs could not be demonstrated due to the low amount of contamination (79 ppb in the influent soil). One limitation of the AER is that it cannot handle two-phase materials such as sludge. Soils should be dried and sized (smaller than 10 mesh) before being fed into the reactor. Another limitation is that other types of incineration processes are more cost effective for high BTU content material. Since no supplementary fuels are required, this process is better suited for low BTU material. A cost estimate guideline is included. Recently the U.S. EPA and the Texas Water Commission jointly issued J.M. Huber Corporation a RCRA permit which authorizes the incineration of any non-nuclear RCRA hazardous waste in the AER.

CONTAMINANTS:

Analytical data is provided in the treatability study report. The breakdown of the contaminants by treatability group is:

<u>Treatability Group</u>	<u>CAS Number</u>	<u>Contaminants</u>
W02-Dioxins/Furans/PCBs	1746-01-6	2,3,7,8-Tetrachloro-dibenzo-p-dioxin
	1336-36-3	Total PCBs

Note: This is a partial listing of data. Refer to the document for more information.

TABLE 1**SUMMARY OF DIOXIN TREATMENT PROCESSES**

<u>Process Name</u>	<u>Performance/Destruction Achieved</u>	<u>Cost</u>
Stationary Rotary Kiln Incineration	Greater than 99.999 DRE demonstrated on dioxin at combustion research facility	\$0.25 - \$0.70/lb for PCB solids
Mobile Rotary Kiln Incineration	Greater than 99.9999 DRE for dioxin by EPA unit; process residuals delisted	NA
Liquid Injection Incineration	Ocean incinerators only demonstrated 99.9 on dioxin-containing herbicide orange	\$200 - \$500/ton
Fluidized-bed Incineration	Greater than 99.9999 DRE demonstrated on PCBs	\$60 - \$320/ton
Infrared Incinerator (Shirco)	Greater than 99.9999 DRE on TCDD-contaminated soil	\$200 - \$1,200 per ton
High Temperature Fluid Wall (Huber AER)	Greater than 99.999 DRE on TCDD-contaminated soil	\$300 - \$600/ton
Molten Salt (Rockwell Unit)	Up to eleven nines DRE on hexachlorobenzene	NA
Supercritical Water Oxidation	99.9999 DRE on dioxin-containing waste reported by developer	\$0.32 - \$2.00/gallon
Plasma Arc Pyrolysis	Greater than 99.9999 destruction of PCBs and CCl ₄	\$300 - \$1,400/ton
In-Situ Vitrification	Greater than 99.9% destruction on PCB-contaminated soil	\$120 - \$250/M ³
Solvent Extraction	Still bottom extraction: 340 ppm TCDD reduced to 0.2 ppm; 60-90% removal from soils.	NA
Stabilization/Fixation	Tests using cement decreased leaching of TCDD	NA
UV Photolysis	Greater than 98.7% reduction of TCDD	\$250 - \$1,200/ton
Chemical Dechlorination APEG processes	Reduction of 2,000 ppb TCDD to below 1 ppb for slurry (batch process)	\$296/ton for in situ, \$ 91/ton for slurry
Biological in situ addition of microbes	50-60% metabolism of 2,3,7,8-TCDD using white rot fungus	NA
Degradation using Ruthenium Tetroxide	Reduction of 70 ppb TCDD to below 10 ppb in 1 hr	NA
Degradation using Chloroiodides	Up to 92% degradation on solution of TCDD in benzene	NA

NOTE: Quality assurance of data may not be appropriate for all uses.

SUPERFUND TREATABILITY CLEARINGHOUSE ABSTRACT

Treatment Process: Physical/Chemical - Dechlorination

Media: Soil/Generic

Document Reference: Alliance Technologies Corp. "Technical Resource Document: Treatment Technologies for Dioxin-Containing Wastes." Technical Report EPA/600/2-86/096. 244 pp. October 1986.

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Site Name: Denny Farm Site, MO (Non-NPL)

Location of Test: Denny Farm, MO

BACKGROUND: This document summarizes several case studies on the applications of the Alkali Polyethylene Glycolate (APEG) treatment process applied to dioxin-contaminated soil. This treatability study compiles available information on those technologies for dioxin containing solids, liquids and sludges, many of which are in early stages of development. A discussion of the APEG technology is contained in this abstract. Other technologies are discussed in Document Numbers FCFR-3 and FCFR-4. Technologies evaluated were those that destroy or change the form of dioxin to render it less toxic. Those technologies not tested on dioxin-containing wastes had been tested on PCB-containing wastes. The report divides the technologies into thermal and non-thermal groups for discussion. It was noted that incineration was the only sufficiently demonstrated technology for treatment of dioxin containing wastes (51 FR 1733) and RCRA Performance Standards for Thermal Treatment require 99.9999 percent destruction removal efficiency (DRE) of the principal organic hazardous constituent (POHC). Factors which affect the selection/use of a particular technology are discussed. Technical performance for treating a specific waste type and costs are both considered in this discussion. A summary of dioxin treatment processes, their performance/ destruction achieved, and estimated costs are provided in Table 1. QA/QC is not discussed.

OPERATIONAL INFORMATION: This document summarized several case studies on the applications of the Alkali Polyethylene Glycolate (APEG) treatment process applied to dioxin-contaminated soil. All data are either bench or pilot scale. Two different molecular weight APEG reagents were used. Three tests were K-400 (potassium-based reagent and polyethylene glycol of average molecular weight of 400) and two tests were K-120. It is unclear whether the waste matrix was a solvent, soil, or contaminated debris. All analyses reported were total waste analyses.

PERFORMANCE: The document concludes that this technology has a potential for treating soil contaminated with dioxins. Efficiencies improve with increased temperature. Costs for the slurry process is estimated at \$91/ton and for the in situ process of \$296/ton.

CONTAMINANTS:

Analytical data is provided in the treatability study report. The breakdown of the contaminants by treatability group is:

<u>Treatability Group</u>	<u>CAS Number</u>	<u>Contaminants</u>
W02-Dioxins/Furans/PCBs	1336-36-3 1746-01-6	Total PCBs 2,3,7,8-Tetrachlorodi- benzo-p-dioxins

Note: This is a partial listing of data. Refer to the document for more information.

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NOTE: Quality assurance of data may not be appropriate for all uses.

Research and Development

980-TS1-RT-FCFR



Technical Resource Document:

Treatment Technologies for Dioxin-Containing Wastes



EPA/600/2-86/096
October 1986

TECHNICAL RESOURCE DOCUMENT
TREATMENT TECHNOLOGIES FOR DIOXIN-CONTAINING WASTE

by

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FOREWORD

As hazardous waste continues to be one of the more prominent environmental concerns to the people of the United States and other countries throughout the world, there are continuous needs for research to characterize problems and develop and evaluate alternatives to addressing those problems. The programs of the Hazardous Waste Engineering Research Laboratory are designed to contribute to satisfying these research needs.

This Technical Resource Document for Treatment Technologies for Dioxin Containing Wastes compiles available information on those technologies. It is intended to provide support for the land disposal prohibition, currently being considered by the EPA, and to provide technical information for those individuals and organizations concerned with the subject waste streams. Those wishing additional information on the various technologies should contact the Hazardous Waste Engineering Research Laboratory.

Thomas R. Hauser
Director
Hazardous Waste Engineering Research Laboratory

FIGURES

<u>Number</u>		<u>Page</u>
3.1	Structure of (a) Dibenzo-p-dioxin and (b) dibenzofuran . .	3-5
4.1.1	Schematic of Rollins Environmental Services' incinerator. .	4-6
4.1.2	Schematic of ENSCO stationary incinerator	4-7
4.1.3	Simplified schematic of CRF rotary kiln	4-10
4.2.1	Schematic of EPA mobile incineration system	4-17
4.2.2	Schematic of ENSCO MWP-2000 mobile rotary kiln incinerator.	4-19
4.3.1	Vertically-oriented liquid injection incinerator	4-33
4.4.1	Cross-section of fluidized bed furnace	4-42
4.4.2	Schematic of circulating bed combustor	4-44
4.5.1	Advanced electric reactor (AER)	4-53
4.5.2	High temperature fluid wall process configuration for the destruction of carbon tetrachloride	4-54
4.7.1	Pyroplasma process flow diagram	4-66
4.8.1	Schematic of generalized molten salt incinerator design..	4-74
4.9.1	Process schematic for oxidation of an aqueous waste with a heating value of 1750 Btu/lb	4-81
4.10.1	Schematic of an in situ vitrification operation	4-89
4.10.2	Schematic of large scale off-gas treatment system	4-91
4.10.3	Cost of in situ vitrification for transuranic wastes as a function of electrical rate and soil moisture	4-94

TABLES

<u>Number</u>		<u>Page</u>
1.1	Dioxin Contaminated Wastes Listed as RCRA Hazardous Wastes, January 14, 1985, 50 FR 1978	1-2
1.2	Summary of Dioxin Waste Sources and Quantities	1-6
1.3	Summary of Treatment Processes	1-7
2.1	Concentrations of Constituents of Concern Which Will Result in Banning Listed Wastes from Land Disposal [51 FR 1732] . .	2-5
3.1	Basis for Listing Wastes [50 FR 1978]	3-2
3.2	Physical and Chemical Characteristics of Some CDDs and CDFs.	3-6
3.3	Physical and Chemical Characteristics of Some Chlorophenols and Chlorophenoxy Compounds	3-10
3.4	Listing of Dioxin Notifiers as of February 18, 1986	3-12
3.5	Constituents of Waste Code F020	3-15
3.6	Constituents of Waste Code F021	3-20
3.7	PCDD and PCDF Concentrations in Manufactured Products and Chemical Intermediates	3-24
3.8	Characterization of Some Soils Contaminated with Dioxin Constituents	3-28
4.1.1	Vertac Still Bottom Test Burn	4-12
4.1.2	Average Unit Costs for PCB Waste Destruction at Permitted Stationary Rotary Kiln Facilities	4-14
4.2.1	Soils Used in the EPA Mobile Incinerator During Preliminary Testing of the Solids Feed System	4-23

TABLES (continued)

<u>Number</u>		<u>Page</u>
4.7.2	Typical Operating Data for PCB Tests (One Hour Runs)	4-70
4.7.3	PCB Test Results	4-71
4.8.1	PCB Combustion Tests in Sodium-Potassium-Chloride-Carbonate Melts	4-77
4.8.2	Summary of Pilot-Scale Test Results	4-78
4.9.1	Composition of Feed Mixtures for Test Runs	4-84
4.9.2	Summary of Results: Oxidation of Organic Chlorides	4-85
4.9.3	Modar Treatment Costs for Organic Contaminated Aqueous Wastes	4-87
5.1.1	Summary of Data Show Percent Removal of TCDD From Contaminated Soils Using APEG Dechlorination Process . . .	5-7
5.1.2	Summary of Data Showing Percent Removal of TCDD From Contaminated Soil at Denny Farm	5-7
5.1.3	Summary of Results of In-Situ Processing - All Soils Initially at 2000 ppb	5-8
5.1.4	Results of Slurry Processing	5-8
5.1.5	Degradation of 2,3,7,8-TCDD Under Different Conditions Using the CDP-Process	5-11
5.1.6	Preliminary Economic Analysis of In Situ and Slurry Processes	5-13
5.2.1	Dissociation Energies for Some Chemical Bonds	5-16
5.2.2	Estimated Volumes and Concentrations of 2,3,7,8-TCDD Produced by the Syntex-IT Photolytic Process	5-20
5.2.3	Design Specifications, Capital, and O&M Costs for 40,000 and 150,000 GPD ULTROX Treatment Plants	5-27
5.3.1	Solubilization of TCDD	5-33
5.4.1	Micro-organisms with Known Capability for Degrading 2,3,7,8-Tetrachlorodibenzo-p-dioxin	5-37

SECTION 1
EXECUTIVE SUMMARY

INTRODUCTION

The 1984 Hazardous and Solid Waste Act Amendments to the Resource Conservation and Recovery Act (RCRA) directed EPA to ban certain dioxin-containing wastes from land disposal unless EPA determines that restrictions on land disposal of these wastes are not needed to protect human health and the environment. Congress, through the 1984 Amendments, fixed a deadline of 24 months from the enactment of the Amendments for EPA to regulate the land disposal of these identified wastes (with some exceptions). In the event that the Agency has not issued regulations by that time (November 1986), land disposal of all specified dioxin-containing waste streams automatically will be banned.

An important aspect of the land disposal restrictions is the identification and evaluation of alternative technologies that can be used to treat the listed wastes in such a way as to meet proposed treatment levels which EPA has determined are protective of human health and the environment. If alternatives to land disposal are not available by November 1986, it may be necessary to extend the deadline for the restrictions on land disposal. The purpose of this document is to identify and evaluate alternative technologies that remove and/or destroy dioxin and related compounds from listed dioxin wastes in order to achieve constituent levels that allow the safe land disposal of the treated residues.

SCOPE

A number of potential technologies exist for treating wastes containing dioxin. Because many of the technologies are currently in early stages of development, it is not possible to fully assess the effectiveness of these

TABLE 1.1. DIOXIN CONTAMINATED WASTES LISTED AS RCRA HAZARDOUS WASTES,
JANUARY 14, 1985, 50 FR 1978

Hazardous Waste from Nonspecific Source		
EPA hazardous waste no.	Hazardous waste	Hazard code
F020*	Wastes** from the production or manufacturing use of tri- or tetrachlorophenol, or of intermediates used to produce their derivatives.**	(H)
F021*	Wastes** from the production or manufacturing use of pentachlorophenol (PCP), or of intermediates used to produce its derivatives.	(H)
F022*	Wastes** from the manufacturing use of tetra-, penta-, or hexachlorobenzene under alkaline conditions.	(H)
F023*	Wastes** from the production of materials on equipment previously used for the production or manufacturing use of tri- or tetrachlorophenols.***	(H)
F026*	Wastes** from the production of materials on equipment previously used for the manufacturing of tetra-, penta-, or hexachlorobenzene under alkaline conditions.*	(H)
F027*	Discarded unused formulations containing tri-, tetra-, or pentachlorophenol or discarded unused formulations derived from these chlorophenols.****	(H)
F028	Residues resulting from the incineration or thermal treatment of soil contaminated with EPA hazardous waste F020, F021, F022, F023, F026, and F027.	(T)

*A proposed regulation [50 FR 37338] would make residues from the incineration of these wastes (if the waste contained less than or equal to 10 ppm TCDD prior to incineration) toxic instead of acute hazardous .

**Except wastewater and spent carbon from hydrogen chloride purification.

***This listing does not include wastes from the production of hexachlorophene from highly purified 2,4,5-trichlorophenol.

****This listing does not include formulations containing hexachlorophene synthesized from prepurified 2,4,5-trichlorophenol as the sole component.

(H) = Acute Hazardous Waste

(T) = Toxic Waste

wastes requiring treatment at this time are wastes such as still bottoms and reactor residues that were generated in the past and remain to be treated. The only process waste stream that is still being generated, and may continue to be generated in the future, is from the manufacture of pentachlorophenol (PCP). However, by far the largest quantity of dioxin-bearing wastes that have been identified are the contaminated soils such as those at Times Beach, Missouri, and various other CERCLA sites throughout the country.

Table 1.2 shows estimated waste quantities for each of the waste codes. Several items associated with the information in the table should be noted. One is that no sources have yet been identified for waste codes F022 and F026. Another is that waste code F028 is not included because it is expected that residues from future incineration of contaminated soil will meet EPA delisting requirements. Finally, contaminated soils are placed in a separate category both because of their unique physical form relative to most process wastes, and also because a large fraction of the contaminated soils are at CERCLA sites whose wastes will not be affected by the RCRA land disposal restrictions until November 1988.

The estimates of the quantities of wastes generated within each waste category in Table 1.2 could have a significant impact on future treatment practices. As shown in the table, there are more than 500,000 metric tons (MT) of dioxin-contaminated soil that may require treatment. This quantity is considerably greater than the estimated maximum 7500 MT of process wastes, such as still bottoms currently requiring treatment and the estimated 2500 MT of industrial process wastes that will be generated in future years. Consequently, it would appear that treatment technologies capable of treating soil wastes are of most importance at this time, particularly those technologies, such as solvent extraction, that are capable of removing the toxic constituents from the soil and thereby reducing the total volume of waste requiring final detoxification/destruction.

TECHNOLOGIES FOR TREATING DIOXIN WASTES

As mentioned previously, a number of technologies for treating dioxin waste are evaluated in this document. A summary of the status of these technologies is provided in Table 1.3. Because studies have shown that dioxin

TABLE 1.3. SUMMARY OF TREATMENT PROCESSES

Process name	Applicable waste streams	Stage of development	Performance/ destruction achieved	Cost	Residuals generated
Stationary Rotary Kiln Incineration	Solids, liquids, sludges	Several approved and commercially available units for PCBs; not yet used for dioxins	Greater than six nines DRE for PCBs; greater than five nines DRE demonstrated on dioxin at combustion research facility	\$0.25 - \$0.70/lb for PCB solids	Treated waste material (ash), scrubber wastewater, particulate from air filters, gaseous products of combustion
Mobile Rotary Kiln Incineration	Solids, liquids, sludges	EPA mobile unit is permitted to treat dioxin wastes; ENSCO unit has been demonstrated on PCB waste	Greater than six nines DRE for dioxin by EPA unit; process residuals delisted	NA*	Same as above.
Liquid Injection Incineration	Liquids or sludges with viscosity less than 10,000 csu (i.e., pumpable)	Full scale land-based units permitted for PCBs; only ocean incinerators have handled dioxin wastes	Greater than six nines DRE on PCB wastes; ocean incinerators only demonstrated three nines on dioxin containing herbicide orange	\$200 - \$500/ton	Same as above, but ash is usually minor because solid feeds are not treated
Fluidized-bed Incineration (Circulating Bed Combustor)	Solids, sludges	GA Technologies mobile circulating bed combustor has a TSCA permit to burn PCBs anywhere in the nation; not tested yet on dioxin	Greater than six nines DRE demonstrated by GA unit on PCBs	\$60 - \$320/ton for GA unit	Treated waste (ash), particulates from air filters
High Temperature Fluid Wall (Huber AER)	Primarily for granular contaminated soils, but may also handle liquids	Huber stationary unit is permitted to do research on dioxin wastes; pilot scale mobile reactor has been tested at several locations on dioxin contaminated soils	Pilot scale mobile unit demonstrated greater than five nines DRE on TCDD - contaminated soil at Times Beach (79 ppb reduced to below detection)	\$300 - \$600/ton	Treated waste solids (converted to glass beads), particulates from baghouse, gaseous effluent (primarily nitrogen)
Infrared Incinerator (Shirco)	Contaminated soils/sludges	Pilot scale, portable unit tested on waste containing dioxin; full scale units have been used in other applications; not yet permitted for TCDD	Greater than six nines DRE on TCDD-contaminated soil	Treatment costs are \$200 - \$1,200 per ton	Treated material (ash); particulates captured by scrubber (separated from scrubber water)

*Not available

(continued)

TABLE 1.3 (continued)

Process name	Applicable waste streams	Stage of development	Performance/ destruction achieved	Cost	Residuals generated
UV Photolysis	Liquids, still bottoms, and soils can be treated if dissolved in first extracted or desorbed into liquid	Full scale solvent extraction/UV process was used to treat 4,300 gallons of still bottoms in 1980; thermal desorption/UV process currently undergoing second field test	Greater than 98.7% reduction of TCDD using solvent extraction/UV process - residual concentration ppm concentrations of TCDD; thermal desorption/UV process demonstrated reduction of TCDD in soil to below 1 ppb	Cost of treating the 4,300 gallons of still bottoms, a solvent using solvent extraction/UV was \$1 million; thermal desorption/UV estimated to cost \$250 - \$1,250/ton extract stream	Solvent extraction/UV process generated treated still bottoms, a solvent extract stream, and an aqueous salt stream; thermal desorption/UV generates a treated soil stream and a solvent extract stream
Chemical Dechlorination-APBC processes	Contaminated soil (other variations of the process used to treat PCB-contaminated oils)	Slurry process currently being field tested at pilot scale; in situ process has been tested in the field	Laboratory research has demonstrated reduction of 2,000 ppb TCDD to below 1 ppb for slurry (batch process); laboratory and field testing of in situ process not as promising	\$396/ton for in situ APBC process; \$91/ton for slurry (batch) process	Treated soil containing chloride salts (reagent is recovered in the slurry process)
Biological Degradation-primarily in situ addition of microbes	Research has been directed toward in situ treatment of contaminated soils - liquids are also possible	Currently laboratory scale-field testing in next year or two	50-60% metabolism of 2,3,7,8-TCDD in a week long period under lab conditions using white rot fungus - reduction to below 1 ppb not achieved	NA	Treated waste medium such as soil or water with TCDD metabolites depending on microorganisms
Chemical Degradation using Ruthenium Tetraoxide	Liquid or soil wastes - possible most effective in decontaminating furniture, other surfaces	Laboratory scale - no work reported since 1983	Reduction of 70 ppb TCDD to below 10 ppb in 1 hr (on soil sample)	NA	Treated medium plus the solvent which has been added (water, CCl_4); TCDD and products not known
Chemical Degradation using Chloroxides	Liquid or soil - thought to be most applicable to decontaminating furniture and buildings	Laboratory scale - no work reported since 1983	Up to 92% degradation on solution of TCDD in benzene - reductions to below 1 ppb were not demonstrated	NA	Treated waste medium; degradation and products are chlorophenols
Gamma Ray Radiolysis	Liquid waste streams (has been applied to sewage sludge disinfection)	Laboratory research; no research currently being conducted	92% destruction of 2,3,7,8-TCDD in ethanol after 30 hours - 100 ppb to 3 ppb	Cost for sewage disinfection facility treating 4 tons per day is \$40 per ton; TCDD treatment would be more expensive	Large chlorinated dioxin molecules are the degradation and products addition to the treated waste medium

Not available

circulating bed variation), the plasma arc process, and the molten salt process. The in situ vitrification process has not shown six nines DRE; however, it is as much a stabilization process as it is a destruction process. Therefore, the primary objective of this technology is to prevent the leaching of dioxin or other toxic constituents from the treated soil; whether the dioxin is driven out of the soil by volatilization or merely contained within the vitrified material is a secondary concern (as long as volatilized dioxin is captured and subsequently destroyed).

Nonthermal technologies evaluated include the following:

- Chemical dechlorination
- Ultraviolet (UV) photolysis
- Solvent extraction
- Biodegradation
- Stabilization/fixation
- Chemical degradation using ruthenium tetroxide
- Chemical degradation using chloriodides
- Gamma ray radiolysis

Of the nonthermal technologies, those that have shown the most promise and the highest level of recent investigation and testing are chemical dechlorination and UV photolysis. Both of these technologies are currently being field tested on dioxin-contaminated soil. As indicated in Table 1.3, preliminary field data on the thermal desorption/UV photolysis process indicate that dioxin was desorbed from soil to a level below 1 ppb, and then destroyed efficiently using ultraviolet radiation. The chemical dechlorination process has also demonstrated a reduction of TCDD in soil to below 1 ppb, but only on a laboratory scale.

The other nonthermal processes have not shown as much promise with regard to treating dioxin waste. Solvent extraction is a potentially useful technology since it could, if successfully applied to soil treatment, reduce the volume of the waste stream that requires final treatment/destruction by several orders of magnitude. Unfortunately, this technology has not yet

associated waste streams are themselves subject to costly treatment processes. Therefore, technologies such as solvent extraction or desorption, which separate the toxic constituents from the waste matrix prior to final treatment should receive further investigation.

Most of the emerging technologies are being designed for operation at the waste source. This trend to portable or field-erected technologies reflects a reaction to public opposition to the transport of dioxin waste from source to waste treatment facilities, and should continue to be encouraged.

In addition, because of the large volume of soil contaminated by relatively low concentrations of dioxin, it is also important to investigate methods of in situ treatment. These methods would limit the handling of the waste so that further dispersion of contaminated materials into the environment is minimized. Most of the technologies in this category, such as biodegradation, in situ vitrification, chemical dechlorination, and stabilization in the near future have not yet been sufficiently demonstrated. Use in the near future seems improbable without more intense development of these technologies. Steps should be taken to encourage these developments.

The treatment of dioxin contaminated liquids and low viscosity sludges does not appear to be as large a problem as is the treatment of contaminated soils. This is primarily because the quantity of liquids and sludges is much lower, and also because the liquid waste form generally calls for less extensive handling and pretreatment. Technologies, such as plasma arc pyrolysis and supercritical water oxidation, appear to be capable of treating these wastes, and their development should be fostered, as should other reasonable activities aimed at the development of emerging technologies.

SECTION 2.0

REGULATIONS CONCERNING MANAGEMENT OF LISTED DIOXIN WASTES

2.1 CURRENT REGULATION UNDER RCRA

Certain dioxin contaminated wastes originally regulated under the Toxic Substance Control Act (TSCA), 40 CFR Part 775, were listed as hazardous wastes under the Resource Conservation and Recovery Act (RCRA) on January 14, 1985, 50 FR 1978. The January 14, 1985 RCRA Amendments list as acute hazardous wastes certain chlorinated dibenzo-p-dioxins, dibenzofurans, and phenols (and their phenoxy derivatives). A complete listing was presented in Table 1.1. When the RCRA Amendment listing dioxin-contaminated wastes became effective on July 15, 1985, duplicate listings of certain dioxins under RCRA and TSCA were revoked.

The inclusion of these dioxin-contaminated wastes under the RCRA regulations was mandated by the RCRA statutory amendments entitled the Hazardous and Solid Waste Amendments of 1984 (HSWA), signed into law November 8, 1984 as Public Law 98-616. HSWA, among other things, mandate a RCRA listing status for 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)-contaminated wastes, stringent technical requirements for land disposal facilities, an expanded definition of land disposal, and various land disposal bans and restrictions.

HSWA state that in the case of any hazardous waste which is prohibited from one or more methods of land disposal, the storage of such hazardous waste is prohibited unless such storage is solely for the purpose of the accumulation of such quantities of hazardous waste as are necessary to facilitate its proper recovery, treatment, or disposal. In order for interim storage of these wastes to be excluded from this prohibition, it must be demonstrated that the storage is solely for the purposes of facilitating proper recovery, treatment, or disposal. HSWA also specify a two year (24 months) period during which EPA must decide whether or not to completely

Pertinent regulatory provisions are summarized below.

- 2,3,7,8-TCDD-contaminated wastes resulting from the production or manufacturing use of several chlorophenols and chlorobenzenes, including contaminated soil, are added to the list of RCRA regulated acute hazardous wastes (RCRA hazardous waste numbers F020, F021, F022, F023, F026, F027, F028); RCRA regulated quantity for small quantity generators is 1 kilogram of 2,3,7,8-TCDD-contaminated material;
- 2,3,7,8-TCDD wastes may be disposed only in fully permitted RCRA (Part B) land disposal facilities (interim status land disposal facilities are not acceptable);
- Interim status facilities that may be acceptable for the management of 2,3,7,8-TCDD wastes include surface impoundments (for wastewater sludge; managed pursuant to 40 CFR 264.231), enclosed waste piles (pursuant to 40 CFR 264.250(c)), tanks (pursuant to 40 CFR 264.200), containers (pursuant to 40 CFR 264.175), incinerators (if certified pursuant to 265.352), and thermal treatment units (if certified pursuant to 265.383);
- A waste management plan is required for all land disposal facilities that submit Part B of their RCRA permit application. The waste management plan will specifically address the means by which the waste will be managed safely at the land disposal facility;
- 2,3,7,8-TCDD wastes may not be stored or disposed of in unlined units;
- Interim status incinerators and interim status thermal treatment units are allowed to burn 2,3,7,8-TCDD wastes if they are "certified" by the Assistant Administrator for the EPA Office of Solid Waste and Emergency Response, pursuant to 40 CFR 265.352 and .383, respectively as meeting 40 CFR Part 264, Subpart O, RCRA performance standards;
- Incinerators and thermal treatment units that are used to burn 2,3,7,8-TCDD wastes must achieve a DRE of 99.9999 percent (i.e., six nines DRE); and
- Residue resulting from incineration or thermal treatment of dioxin-containing soils (F028) must be, at a minimum, managed at a RCRA interim status land disposal facility.

TABLE 2.1. CONCENTRATIONS OF CONSTITUENTS OF CONCERN WHICH WILL RESULT
IN BANNING LISTED WASTES FROM LAND DISPOSAL [51 FR 1732]

Constituent*	Screening level (mg/l)
2,3,7,8-TCDD	4×10^{-9}
Other TCDDs	4×10^{-7}
2,3,7,8-PeCDDs	8×10^{-9}
Other PeCDDs	8×10^{-7}
2,3,7,8-HxCDDs	1×10^{-7}
Other HxCDDs	1×10^{-5}
2,3,7,8-TCDFs	4×10^{-8}
Other TCDFs	4×10^{-6}
2,3,7,8-PeCDFs	4×10^{-8}
Other PeCDFs	4×10^{-8}
2,3,7,8-HxCDFs	4×10^{-7}
Other HxCDFs	4×10^{-5}
2,4,5-Trichlorophenol	8.0
2,4,6,-Trichlorophenol	0.04
2,3,4,6-Tetrachlorophenol	2.0
Pentachlorophenol	1.0

*Definitions of abbreviations used above

TCDDs and TCDFs = All isomers of tetrachlorodibenzo-p-dioxins and
-dibenzofurans respectively.

PeCDDs and PeCDFs = The pentachlorodibenzo-p-dioxins and -dibenzofurans.

HxCDDs and HxCDFs = The hexa-isomers.

SECTION 3.0

CHARACTERIZATION AND QUANTIFICATION OF LISTED DIOXIN WASTES

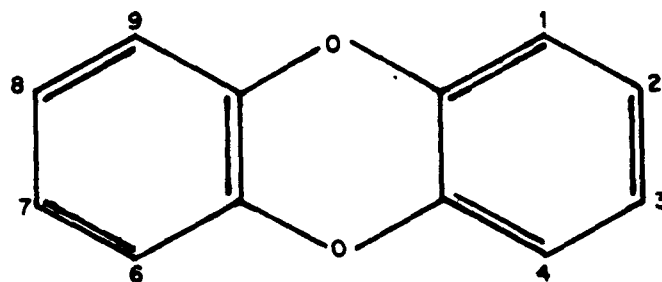
3.1 INTRODUCTION

The purpose of this section is to characterize the wastes described by RCRA codes F020, F021, F022, F023, F026, and F027. These codes describe wastes from the production and manufacturing use of tri-, tetra-, and pentachlorophenols and from the manufacturing use of tetra-, penta-, and hexachlorobenzenes under alkaline conditions and elevated temperatures. These wastes include still bottoms, reactor residues, untreated brines, spent filter aids, spent carbon adsorbents, and sludges resulting from wastewater treatment. They also include wastes resulting from the production of materials on equipment previously used for the production and manufacturing of tri- and tetrachlorophenols, and formulations containing these chlorophenols and their derivatives. Waste code F028 is a treatment residue from incineration or thermal treatment of dioxin-containing soil to six nines DRE. It is designated a toxic and not an acute hazardous waste, and therefore is not addressed in this document. The untreated soils, however, that have been contaminated by spills of wastes in codes F020, F021, F022, F023, F026 and F027 are defined as hazardous (50 FR 28713) and are addressed.

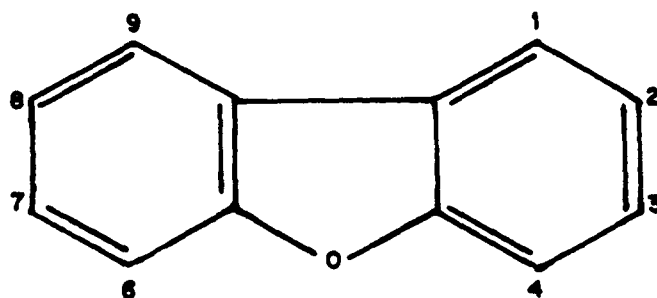
As shown in Table 3.1, the basis for listing each of these wastes and for banning them from land disposal is the expected or known presence of significant quantities of tetra-, penta-, and hexachlorodibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs). These compounds are among the most potent animal carcinogens known and are potential human carcinogens in addition to being extremely persistent in the environment. These wastes may also contain significant concentrations of tri-, tetra-, and pentachlorophenols and their chlorophenoxy derivatives, some of which are potential human carcinogens (2,4,6-TCP) and/or are suspected of causing liver and kidney damage (U.S. EPA, 1985).

TABLE 3.1 (continued)

EPA code	Waste code description	Hazardous constituents for which listed
F023	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials on equipment previously used for the production or manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tri- and tetrachlorophenols. (This listing does not include wastes from equipment used only for the production or use of hexachlorophene from highly purified 2,4,5-trichlorophenol).	Tetra-, and pentachlorodibenzo-p-dioxins; tetra- and pentachlorodibenzofurans; tri- and tetra-chlorophenols and their chlorophenoxy derivative acids, esters, ethers, amines, and other salts.
F026	Wastes (except wastewater and spent carbon from hydrogen chloride purification) from the production of materials on equipment previously used for the manufacturing use (as a reactant, chemical intermediate, or component in a formulating process) of tetra-, penta-, or hexachlorobenzene under alkaline conditions.	Tetra-, penta-, and hexachlorodibenzo-p-dioxins; tetra-, penta-, and hexachlorodibenzofurans.
F027	Discarded formulations containing tri-, tetra-, or pentachlorophenol or discarded formulation containing hexachlorophene synthesized from prepurified, 2,4,5-trichlorophenol as the sole component.	Tetra-, penta-, and hexachlorobibenzo-p-dioxins; tetra-, penta-, and hexachlorodibenzofurans; tri-, tetra-, and pentachlorophenols and their chlorophenoxy derivative acids, esters, ethers, amines, and other salts.
F028	Residues resulting from the incineration or thermal treatment of soil contaminated with EPA Hazardous Waste Nos. F020, F021, F022, F023, F026, and F027.	Tetra-, penta-, and hexachlorodibenzo-p-dioxins; tetra-, penta-, and hexachlorodibenzofurans; tri-, tetra-, and pentachlorophenols and their chlorophenoxy derivative acids, esters, ethers, amines, and other salts.



(a) Dibenzo-p-Dioxin



(a) Dibenzofuran

Figure 3.1. Structure of (a) Dibenzo-p-Dioxin and (b) Dibenzofuran
Source: Environment Canada, 1985

- low vapor pressure;
- absorption of ultraviolet radiation; and
- low rate of biodegradation.

PCDDs are characterized by low polarization which results in a very low water solubility, but a much higher solubility in organic solvents. The water solubility of 2,3,7,8-TCDD has been measured by a number of investigators. Recently derived estimates have been in the range of 7 to 20 parts per trillion. In contrast, the solubility of TCDD in organic solvents such as benzene, xylene, and toluene ranges from 500 to 1,800 ppm. This results in a log octanol/water partition coefficient of up to nine. Consequently, in the environment TCDD is not generally found at high concentrations in aqueous media. Instead, it is bound to the organic matter in soil where it may remain for long periods of time. The half-life of TCDD in soil has been estimated to range between 1.5 and 10 years (U.S. EPA, 1985), but the results of one recent study indicated virtually zero degradation of TCDD after being in the soil for twelve years. In addition, the TCDD had only moved about 10 centimeters over this period of time (Freeman & Schroy, 1986).

Another property of TCDD is that it absorbs ultraviolet light strongly with a wavelength of maximum absorption lying within the sunlight region (above 290 nm). As a result, TCDD has been shown to degrade significantly when exposed to light of this wavelength in the presence of a hydrogen donor such as hexane or some other organic solvent. Tests have shown that when a hydrogen donor is not present, degradation of TCDD is negligible (Crosby, D. G., 1985). Photolytic degradation was applied to 4,300 gallons of still bottoms containing 343 ppm of 2,3,7,8-TCDD. The dioxin was first extracted from the still bottoms using hexane, and then the extract was irradiated with ultraviolet light; 99.9 percent destruction of TCDD was achieved. This process will be described in more detail in Section 5.

One of the most important properties of TCDD with respect to treatment is that it is destroyed at temperatures between 1200 and 1400°C (Shaub and Tsang, 1982). When chlorinated compounds are incinerated at lower temperatures, however, dioxins may be formed in large quantities. The heat of combustion of PCDD is 2.81 kilocalories per gram which is greater than the heat of combustion of compounds such as 1,1,1-trichloroethane and pentachlorophenol.

Chlorophenols and Chlorophenoxy Compounds

In general these compounds are water soluble, and in wastes they concentrate in the aqueous phase where they are biodegradable by adapted microorganisms (U.S. EPA, 1985). The biodegradation half-life of 2,4,5-T and Silvex in water is expected to be one to three weeks. The same compounds have a similar half-life due to biodegradation in soils. 2,4,5-TCP, however, has been shown to be persistent in some soils. In one case, where the initial concentration of 2,4,5-TCP in soil was 5000 ppm, the concentration after three years was still 1 to 20 ppm (Lautzenheiser, 1980).

Other properties of these compounds include relatively low volatility, ability to be adsorbed by organic matter such as activated carbon, and susceptibility to photolytic degradation (U.S. EPA, 1985; Lautzenheiser, 1980). Chemical and physical characteristics of these compounds are listed in Table 3-3.

3.3 WASTE SOURCES, QUANTITIES, AND COMPOSITION

3.3.1 Sources of Data

The primary source of data utilized for waste quantity estimates was a report prepared by Technical Resources, Inc. (TRI), entitled, "Analysis of Technical Information to Support RCRA rules for Dioxins - Containing Waste Streams". This report evaluated previous estimates of waste quantities made by Radian (Radian, 1984), and determined that they reflected past practices. TRI presented revised waste generation quantities based on more current information on manufacturing processes obtained by talking to industry contacts. Their estimates appear to be the best available at this time; however, where additional information was available, changes have been made to their estimates.

There are several other sources of data which may be used in the future to obtain better estimates of the quantity of waste containing dioxin. One of these is EPA's Dioxin Strategy. Tiers one, two and three of the Dioxin Strategy encompass sites where 2,4,5-TCP and its pesticidal derivatives were produced or formulated and also sites where wastes from these processes were disposed. Close to 100 potential sites were identified in Tiers 1 and 2

(Radian, 1984); a report will be issued in the near future containing information related to the extent of contamination at these sites. The information in this report will hopefully contain data which will allow for a better estimate of waste quantities and characteristics, particularly for those sites where waste was disposed (Korb, 1986).

Another potential but unused source of data is RCRA Biennial Reports. These reports are filed biennially by hazardous waste treatment, storage and disposal facilities. EPA has indicated that the data from the 1983 reports are not very accurate both because of a poor response rate, and also because data reported to states were not carefully verified prior to sending data summaries to EPA headquarters (Stoll, 1986). In addition, at the time of the 1983 report, the dioxin waste codes (F020-F028) had not yet been developed. Consequently, the 1983 report only contained data concerning the "U" waste codes for tri-, and tetra-, and pentachlorophenol and their pesticide derivatives 2,4,5-T and Silvex. These waste codes have now been replaced by F027. The 1985 Biennial Reports will contain data on the quantities of waste in codes F020-F028 that were treated, stored or disposed in 1985. These data should be available in the fall of 1986. Whether these data will be better than the data from the 1983 Biennial Reports is unknown at this time.

Finally, facilities that handle (generate, store, treat, or dispose) wastes covered under the dioxin listing rule were required to notify EPA by April 15, 1985. Information contained in the notifications does not at this time include data on the quantities of waste generated or stored, but it does indicate which waste codes the facility handles, and it also includes data to indicate the waste treatment and storage capacity at these facilities. TRI utilized this information to estimate the quantities of F027 waste that will require treatment.

A recent listing of the dioxin waste notifiers is presented in Table 3.4. This listing is updated monthly as new facilities notify, or as facilities that do not belong on the list are deleted. It is expected that information regarding the quantities of wastes handled by these facilities will be assembled in the future.

3.3.2 Waste Code F020

Sources of Waste--

This waste code includes wastes from the production and manufacturing of tri- or tetrachlorophenols or intermediates used to produce their derivatives. The major derivatives include phenoxy compounds such as 2,4,5,-trichlorophenoxyacetic acid (2,4,5,-T), 2-(2,4,5-trichlorophenoxy) propionic acid (Silvex), and hexachlorophene.

The manufacture of 2,4,5-TCP is accomplished by the alkaline hydrolysis of tetrachlorobenzene. The primary wastes from the process include distillation bottoms from solvent recovery, spent filter aids, and reactor bottoms. These wastes, in addition to the product itself, will be contaminated with CDDs, CDFs and chlorophenols. The amount of CDDs formed in the process is dependent upon reaction temperature, which in turn is dependent upon the solvent used (methanol, ethanol, ethylene glycol, toluene or isomyl/amyl alcohols). When methanol or water are used as the solvent, the process operates at around 220-300°C, a temperature at which lab experiments have shown the formation of 1.6 g TCDD per kg of 2,4,5-TCP. Using ethylene glycol the process operates at lower temperatures and CDD formation should be lower (U.S. EPA, 1985).

2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol are most efficiently produced by the chlorination of phenol. In this process more 1,3,6,8-TCDD than 2,3,7,8-TCDD is formed. These products also contain up to 50 ppm of CDFs.

The manufacture of 2,4,5-T and other phenoxy compounds utilize 2,4,5-TCP as one of their starting materials. Since TCDD contaminates 2,4,5-TCP, and may also be generated in the formation of the phenoxy compound itself, it is expected to be present in both the product and the wastes from its manufacture. Phenoxy herbicides such as 2,4,5-T and Silvex are synthesized by reacting the appropriate chlorophenol with a haloalkanoic acid under alkaline reflux conditions. These conditions are conducive to the formation of CDDs and CDFs. Careful control of reaction time, temperature, and pH are said to have an effect in reducing the formation of TCDDs. Wastes from the process include caustic scrubber water, spent filter aids and/or carbon adsorbent, and distillation bottoms from solvent recovery. Solvents used are similar to those used in the production of 2,4,5-TCP. Formerly methanol was used, and more recently a mixture of ethylene glycol and toluene or xylene was used.

TABLE 3.5. CONSTITUENTS OF WASTE CODE F020

Source	2,3,7,8-TCDD	TCDDs	Other CDDs	CDFs	Other Possible Constituents	References
Herbicide Manufacture (still bottoms, and reactor residues from the manufacture of 2,4,5-T, 2,4,5-TCP and Hexachlorophene)	60-1290 ppm	0.6-350 ppm			<ul style="list-style-type: none"> • Methanol • Toluene • Xylene • ethylene glycol ethanol • 2,4,5-TCP • trichloroanisoles (methoxyphenyls) • tetrachloro-benzene 	des Rosiers, 1985; Radian, 1984; U.S. EPA, 1985 30-50% 1-10% 55% 0-0.5%
Non-Aqueous Phase Leachate (from disposal of waste from manufacture of 2,4,5-T and phenoxy herbicides - Love Canal, Hyde Park)	0.2-20.2 ppm				<ul style="list-style-type: none"> • similar to wastes described above plus: • heavy metals <ul style="list-style-type: none"> - antimony - arsenic - lead - mercury - aluminum - chromium • fluoroorganics • bromoorganics • phosphides • sulfides • PCB 	U.S. EPA, 1985 100-1000ppm
Filter Aids in 2,4,5-TCP manufacture		0.008-300 ppm			<ul style="list-style-type: none"> • Inorganic Solids • chlorophenols 	U.S. EPA, 1985 99.5% 0-0.5%
Filter Cake from Hexachlorophene manufacture		8-2000 ppb			<ul style="list-style-type: none"> • Inorganic Solids • chlorophenols or organic solvents 	U.S. EPA, 1985 99.5% 0.05%
Spent Carbon from treatment of aqueous leachate	untreated waste, 0.004-0.017 ppb; treated waste, 0.010 ppb				<ul style="list-style-type: none"> • Spent Carbon • chlorophenols and other organics 	U.S. EPA, 1985 99.5% 0.05%

spent carbon from the treatment of aqueous phase leachate from the Love Canal Landfill. The TRI report did not include an estimate of the quantity of spent carbon from treatment of aqueous phase leachate at the Hyde Park Landfill. EPA Region II personnel have indicated that there are currently several dumpsters of spent carbon at the site that Calgon (the manufacturer of the carbon) will not accept for regeneration because of possible dioxin contamination. Aqueous phase leachate is still being generated at a rate of approximately 5000 gallons per day, so spent carbon will also continue to be generated and require treatment (Gianti, 1986).

In addition to the non-aqueous phase leachate that is currently stored in lagoons at Hyde Park, an additional 40 to 200 gallons per day are continuing to be collected. At an average rate of 120 gallons per day, 200 MT would be collected in one year. The period of time over which NAPL will continue to be generated is not known (Gianti, 1986).

In addition to these major sources of waste, there are probably other smaller sites where 2,4,5-TCP and derivatives were manufactured or formulated in the past and wastes are currently stored. Possible locations of these sites have been and are being identified through EPA's Dioxin Strategy and also through the provision that all potential handlers of dioxin wastes notify EPA of their activities. Data on the quantity of wastes at these "other" sites, however, are not currently available. TRI estimated that the quantity of F020 waste at these miscellaneous sites is 500 MT.

3.3.3 Waste Code F021

Sources of Waste--

This waste code encompasses wastes from the production and manufacturing of pentachlorophenol. Pentachlorophenol (PCP) and its sodium salt have various uses as fungicides and biocides with the majority (80 percent) being used as a wood preservative. Since all non-wood uses of PCP will be banned as a result of a notice of intent to cancel made by EPA on January 8, 1986 (Chemical Regulation Reporter, 1/10/86), it is expected that all future uses will be as a wood preservative.

The manufacture of pentachlorophenol can be accomplished either by the chlorination of phenol or by the alkaline hydrolysis of hexachlorobenzene. In the United States, the former method is used. The chlorination usually

formation of PCDDs and PCDFs (des Rosiers, 1985). The number of sites containing these sludges may exceed 100; however, no estimates of the quantity of sludges has been made. In addition, 23 damage incidents related to wood treating operations using PCP were included in the Listing Background Document. These damage incidents include cases where sludges and wastewaters were stored onsite and contaminated soil and water. This waste stream is being included in this discussion due to its possible listing as a "dioxin waste" to be banned from land disposal.

Waste Characteristics--

As mentioned above, the manufacture of PCP does not currently generate a waste stream containing CDDs. In the future, however, PCP will have to be purified to reduce HCDD concentrations from 15 ppm to 1 ppm. Radian estimated the composition of a waste stream generated as a result of the purification of PCP by distillation (Radian, 1984). This waste stream would consist primarily of organic solids (nonvolatile), various chlorinated phenols and organic solvents as indicated in Table 3.6. In addition, a small fraction of the waste would consist of residual catalyst (aluminum chloride), and total CDDs could reach 2,000 ppm. Future purification of PCP will probably not be by distillation, but instead by a solvent extraction and crystallization process. The wastes from this process are assumed to be similar to those generated by distillation (TRI, 1985).

Waste from wood treatment facilities is expected to contain a large variety of constituents. The exact composition of the waste will vary from facility to facility, but in all cases will be a sludge with varying concentrations of water, chlorophenols, and creosote. Organometallic compounds such as copper and zinc naphthalenates and arsenicals are also expected to be potential constituents, in addition to PCBs and waste solvents. The source of CDDs and CDFs in these wastes would be from the inherent contamination of PCP with these compounds. Higher concentrations may be present if waste pits and lagoons containing these wastes were torched to reduce volume.

Waste Quantities--

The only current manufacturer of PCP is Vulcan Materials Company. Previous manufactures include Dow, which ceased production in 1980, and Reichhold Chemicals, Inc. which ceased production in 1985 (TRI, 1985). TRI estimated that Vulcan would fill the current U.S. demand for PCP of 15,000 MT per year. If this is the case, and if purification results in a waste stream of 5 percent of the end product, the quantity of waste generated through purification will be 750 MT per year.

Wastes from formulation of PCP are not expected to be generated in the future since all PCP is expected to be sold directly to wood preservers. Previous to the ban of non-wood uses of PCP, however, 20 percent of the PCP was formulated into products for herbicidal, antimicrobial, and disinfectant use (Chemical Regulation Reporter, 1/10/86). These uses are assumed to have resulted in the generation of 350 MT per year of scrubber water sludges contaminated with PCP and HCDD. Three hundred fifty MT are estimated for the past years (1985) formulation activities, and another 350 MT for the current years activities. Therefore, as indicated previously in Table 1.2, 700 MT of waste code F021 presently require treatment.

3.3.4 Waste Code F022

The Radian Report (Radian, 1984) states that there are no known commercial activities with the processes encompassed by this waste code. The compound, 2,4,5-trichlorophenol, was manufactured by the alkaline hydrolysis of tetrachlorobenzene which would subject its wastes to inclusion in this waste code, in addition to waste code F020. Since 2,4,5-TCP is not being manufactured at this time, no wastes are currently being generated. Potentially generated wastes, and wastes generated by this process in the past are discussed previously under waste code F020.

3.3.5 Waste Code F023

Sources of Waste--

Production trains are often used for the production of chemicals whose manufacture necessitates the use of similar process equipment. In the manufacture of chemicals on a production train previously contaminated with

currently using contaminated equipment and generating contaminated wastes. In addition, they assumed that current production levels are equal to the greatest past production levels. These assumptions would seemingly lead to an upper bound estimate of the quantity of F023 waste generated. The actual quantity probably lies between TRI's estimate of zero and Radians estimate of 573 MT per year.

3.3.6 Waste Code F026

The only manufacturing process that involves the manufacturing use of tetra-, penta-, or hexachlorobenzenes is the manufacture of 2,4,5-Trichlorophenol. As mentioned above, the manufacture of 2,4,5-TCP involves the alkaline hydrolysis of tetrachlorobenzene. Wastes from the production of materials on equipment previously used to manufacture 2,4,5-TCP, however, is regulated under waste code F023. Consequently there should be no F026 waste generated..

3.3.7 Waste Code F027

Sources of Waste--

This waste code encompasses discarded, unused formulations of tri-, tetra-, and pentachlorophenols and their derivatives. These wastes arise either because the product is off specification, the product was manufactured but then its use was banned, or an excess amount was produced or acquired. Because most of these compounds are no longer being manufactured, these wastes are not currently being generated. The exception to this, as mentioned above, is pentachlorophenol which is still manufactured, and so wastes from unused formulations may continue to be generated. For the other compounds of concern unused formulations which have been generated in past years may still lie in storage and eventually require final destruction/disposal.

Waste Characteristics--

Measured concentrations of CDDs and CDFs in the products of concern are presented in Table 3.7. As indicated by the data in this table, the concentration of CDDs in these products can range from non-detectable levels

up to hundreds of ppm. The actual concentration will vary from batch to batch, and compound to compound. In addition, the products may have contained higher concentrations of CDDs in the past than they have more recently. For example, the mean concentrations of 2,3,7,8-TCDD in Agent Orange and Agent Purple (both mixtures of 2,4,5-T and 2,4-D) in the 1960s were 1.98 and 32.8 ppm respectively (Young, 1983) while it was claimed that those prepared in the 1970s contained less than 0.1 ppm (Rappe, 1979). Despite this claim there may still remain quantities of waste in storage with substantial levels of TCDD. For example, the Tennessee Valley Authority (TVA) currently has 21 drums of herbicide orange, one of which contains 5.6 ppm of 2,3,7,8-TCDD (TRI, 1985).

The only F027 waste being generated on an ongoing basis would be unused pentachlorophenol. Because of the consent decree requiring PCP manufacturers to reduce the concentration of HCDD in their product from 15 ppm to 1 ppm, this waste will be of less concern than it has been in the past, since the majority of the HCDD will be incorporated in the purification wastes.

The physical forms of these wastes will vary from case to case. Pentachlorophenol is commonly applied to wood as a 5 percent suspension in fuel oil (sometimes blended with creosote) or dissolved in an organic solvent (Chemical Products Synopsis, 1983). The other products are generally marketed as emulsifiable concentrates. These concentrates are prepared by dissolving the active ingredient (15-80 percent) and a surface active agent (less than 5 percent) in a water emulsifiable organic solvent. The surface active emulsifiers are generally polyethylene and polypropylene glycols, calcium sulfonates or various soaps (Sitig, 1980).

Waste Quantities--

TRI estimated the quantity of waste code F027 in storage to be 1,000 MT per year. This estimate was based on a review of data contained in the Dioxin Waste Notifications. They estimated that the amount of waste generated that would place a demand on treatment capacity was equivalent to the storage capacity at facilities notifying EPA that they were handling waste code F027. Their estimate does not include facilities which reported capacity for waste treatment within the plant site because the waste generated at these facilities would not place a demand on offsite treatment.

Large quantities of contaminated soils and sediments also exist in New York State. Two landfills, Hyde Park and Love Canal, were used for the disposal of organic solvents and wastes from the production of chlorophenols and phenoxy herbicides. The Hyde Park landfill is estimated to contain approximately 120 kg of TCDD; leakage of wastes from these landfills has resulted in the contamination of surrounding soils and sediments. It is believed that there are 55,000 cu yds of stream bed sediments contaminated with an average of 70 ppb of TCDD (USEPA, 1985).

Waste Characteristics--

Waste soils, sediments and other solid materials that have been contaminated with dioxin may have varied compositions and concentrations of dioxin. As indicated in Table 3.8 concentrations of TCDD in soils and other solids range from nondetectable (ND) to greater than 26 ppm. The contaminated materials at some of the sites include not only granular materials such as soils and sand, but also asphalt, vegetation, rocks and gravel. These materials may require special procedures to remove and/or destroy the TCDD. Incinerators many times require the feed material to be of a certain size and consistency. Consequently, some sort of pretreatment to reduce size and produce a more uniform feed may be necessary for the treatment of these wastes.

One of the most significant characteristics of TCDD on soils is its very high soil/water partition coefficient. As shown in Table 3.2 the log of the partition coefficient can be as high as seven. The conclusions of a recent study indicate that the most important factor affecting both the concentration of TCDD in soils, and its partitioning between soil and water is the presence of other organics in the soil. The data indicated that in soils with higher concentrations of solvent-extractable organics (particularly halogenated semivolatiles) the TCDD concentrations in water extracts were greater. They further suggested that it is other organic contaminants in the wastes and not the total organic carbon and clay content of soils that affects the mobility of TCDD (Jackson, D. R. et al, 1985). This would mean that in cases where wastes from the manufacture of chlorophenols or chlorophenoxy herbicides were disposed or leaked into soil media along with other organic wastes, TCDD may be much more mobile than would be normally expected. In cases where chlorophenols and organic solvents are not present in the wastes, the TCDD may be much more strongly bound to the soil, and much more difficult to desorb.

Waste Quantities--

It has been estimated that there are 500,000 MT of dioxin-contaminated soils in Missouri, 160,000 MT at Times Beach alone (Radian, 1984). Radian made a rough estimate of the total quantity of dioxin-contaminated soil in the U.S. by assuming an average site size (5 acres with a 1.5 ft. depth) and multiplying this by the number of tier 1, 2, and 3 sites identified in the Dioxin Strategy. Their result was 2.3 million MT. Because of the uncertainties in making an estimate such as this, 500,000 MT was used as the minimum quantity of dioxin-contaminated soils currently requiring treatment in the United States. This is the number that is presented in Table 1.2. It will be possible to make a more accurate estimate of the quantity of contaminated soil after the sites identified in the Dioxin Strategy are better characterized.

Wastes which are of concern for this document are those containing an extractable TCDD or TCDF concentration of greater than 1 ppb. It is possible that much of the contaminated soil will contain strongly adsorbed TCDD, and so will not require treatment with respect to the land disposal ban.

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SECTION 4

THERMAL TECHNOLOGIES FOR LISTED DIOXIN WASTES

In this report, thermal technologies include incineration, pyrolysis and other processes in which heat is the major agent of destruction. As mentioned in Section 3, laboratory studies have shown that CDDs break down rapidly when subjected to temperatures above 1,200°C. As a result, high temperature incineration and other thermal methods have received much attention with regard to treatment of waste containing CDDs. This attention has led to the development by EPA of a mobile incineration system designed specifically for research on wastes containing dioxin and other toxic substances. This mobile incinerator has demonstrated greater than six nines (99.9999 percent) destruction and removal efficiency (DRE) of wastes containing CDDs, and has led EPA to propose in their January 14, 1986 ruling on land disposal of waste containing dioxins (FR, Vol. 51, No. 9) that incineration (or an equivalent thermal technology) be used as the treatment technology for these wastes.

Incineration and other thermal treatment of RCRA-listed dioxin wastes (codes F020, F021, F022, F023, F026, F027) must be done in accordance with the criteria specified under 40 CFR Parts 264.343 and 265.362 in the dioxin listing rule. These criteria specify that processes burning these wastes must achieve a DRE of 99.9999 percent for each principal organic hazardous constituent (POHC) designated in its permit. DRE is determined from the following equation:

$$DRE = \frac{(W_{in} - W_{out})}{W_{in}} \times 100$$

where: W_{in} = mass feed rate of one POHC in the waste stream feeding the incinerator; and

W_{out} = mass emission rate of the same POHC present in exhaust emissions prior to release to the atmosphere.

This section includes subsections on a variety of thermal technologies. Methods of incineration include:

- Stationary Rotary Kiln
- Mobile Rotary Kiln
- Liquid Injection
- Fluidized Bed
- Infrared

Other thermal destruction technologies include:

- High Temperature Fluid Wall
- Plasma Arc
- Molten Salt
- In Situ Vitrification
- Supercritical Water Oxidation

Each subsection contains a process description, an evaluation of the performance of the technology with regard to chlorinated dibenzo-p-dioxins (CDDs) or similar compounds, an assessment of treatment costs, and a discussion of the status of the technology. Not all of these units have been tested using dioxin waste, but most of them have at least been tested using PCB waste; in these cases, the PCB data have been presented as evidence of their performance.

4.1 STATIONARY ROTARY KILN INCINERATION

Several commercial rotary kilns have been permitted to burn PCB wastes. In so doing they have demonstrated six nines DRE for PCBs, and therefore have the potential to burn dioxin wastes. These units are: the Rollins incinerator in Deer Park, Texas; the SCA incinerator in Chicago, Illinois; and the ENSCO incinerator in El Dorado, Arkansas. None of these units has been demonstrated using dioxin wastes; however, the EPA Combustion Research Facility in Jefferson, Arkansas, which operates a rotary kiln incinerator, recently conducted test burns of dioxin wastes. Even though this is not a commercial incineration facility, the data that were generated by the dioxin burns are included to indicate the performance of a rotary kiln.

Rollins (Rollins, 1985; M. M. Dillon, 1983; Gregory, 1981)--

The configuration of the Rollins stationary incinerator is shown in Figure 4.1.1. Solids or sludges are conveyed to the rotary kiln in fiber drums or 55 gallon metal drums. Certain solids (such as capacitors) need to be preshredded prior to being fed into the kiln. Liquid wastes can be fed directly into the afterburner section. The liquids are atomized using compressed air, which produces a rotary action in the combustion zone.

The combustor is a Loddby furnace measuring 1.6m diameter by 4.9m long. The afterburner zone measures 4 x 4.3 x 10.6m. Natural gas and/or No. 2 fuel oil are used as ignition fuel and also as a supplementary fuel if necessary. Combustor temperatures can reach 1500°C, and afterburner temperatures average 1300°C. Residence times in the afterburner range from 2 to 3 seconds. Kiln residence times vary widely according to the form of the waste, with residence time being a function of design, solids content and viscosity. Combustion gases from the afterburner pass through a combination venturi scrubber/absorption tower system in which particulates and acid gases are removed from the gas stream. A fraction of the scrubbing water is dosed with lime and returned upstream of the venturi throat to increase scrubbing efficiency. Induced draft fans are used to drive the scrubber gas stream to the atmosphere.

ENSCO (M. M. Dillon, 1983; McCormick, 1986)--

A schematic of the ENSCO incineration facility is shown in Figure 4.1.2. Drummed wastes are fed to an enclosed shredder where solids drop into a hopper and are conveyed by an auger into the rotary kiln. Liquid wastes are mixed with the shredded solids and conveyed to the kiln or injected directly into the combustion chamber. The air in the enclosed shredder is drawn by a fan into the rotary kiln.

The rotary kiln measures 2.1m in diameter by 10.4m long and is angled slightly so that the solid residue flows by gravity to the ash drop. Flue gases from the kiln are ducted to the 85 cubic meter combustion chamber where fuel (often an organic waste) is burned to create a high temperature zone (outlet temperature 1250°C). This afterburner, which possesses an outlet

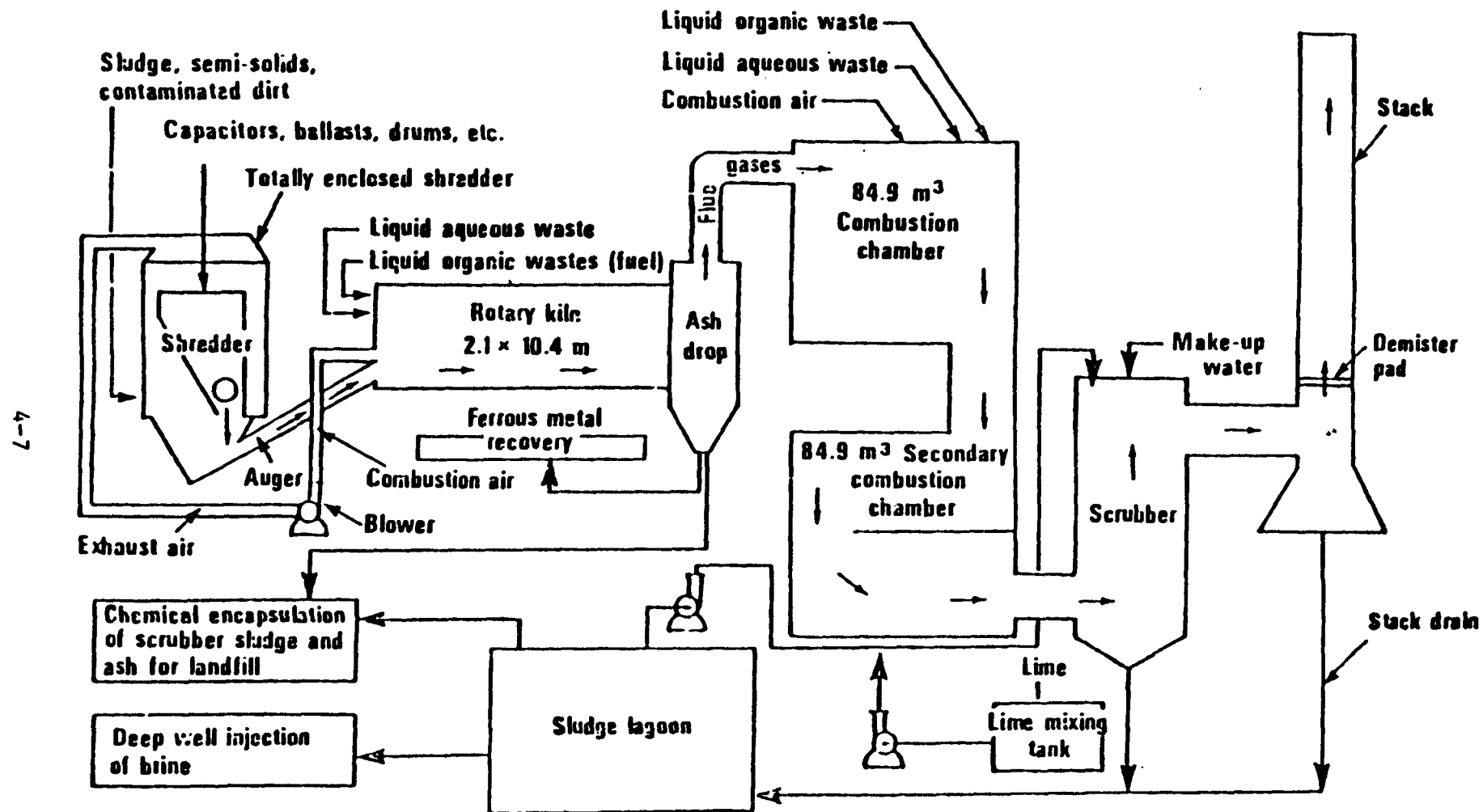


Figure 4.1.2. Schematic of ENSCO stationary incinerator [M.M. Dillon, 1983].

4.1.2 Technology Performance Evaluation

As discussed in the previous subsection, three commercial-scale stationary rotary kiln incinerators have demonstrated six nines DRE (99.9999%) for PCBs and are permitted to burn PCBs. Trial burns of dioxin wastes have not been conducted at any of the commercial-scale stationary rotary kiln incinerators due to strong public opposition. However, trial burns of dioxin-containing wastes have been performed using the stationary rotary kiln incinerator at the U.S. EPA Combustion Research Facility (CRF) in Jefferson, Arkansas.

The CRF is a 3100 sq.ft. permitted experimental facility built for the purpose of conducting pilot scale incineration burns and evaluating whether incineration is an effective treatment/disposal option for various types of hazardous waste. During September 1985, trial burns were conducted at the CRF using dioxin-containing toluene still bottoms (Ross, et al., 1986). These were generated by the Vertac Chemical Company in Jacksonville, Arkansas and stored there pending an EPA decision on appropriate treatment/disposal.

The CRF contains two pilot-scale incinerators and associated waste handling, emission control, process control, and safety equipment (Carnes, 1984). Additionally, onsite laboratory facilities are available to characterize the feed material and process performance samples. As shown in Figure 4.1.3, the main components of the CRF incineration system include a standard rotary kiln incinerator, an afterburner and a conventional air pollution control system (Carnes, 1984; Ross, et al., 1986; Ross, et al., 1984). Waste fed into the kiln flows countercurrent to the primary burner (concurrent configuration is also possible). The monitoring/control equipment for the kiln includes a propane meter, a pitot tube to monitor primary combustion air, a shielded thermocouple to control temperature, and monitoring equipment for combustion gas composition and flow rate. Organic components are determined by extractive sampling through a heat-traced sampling line and a liquid impinger (from EPA Method 5) or a volatile organic sampling train (VOST) (Carnes, 1984; Ross, et al., 1986; Ross, et al., 1984).

Following combustion in the kiln, the combustion gases are directed through a refractory-lined transfer duct to the afterburner. A shielded thermocouple is used to control temperature in the afterburner. Surface temperature, exit gas temperature and combustion gas composition and flow rate are monitored. Exhaust gases are cleaned in the air pollution control system which consists of a variable throat venturi scrubber, a fiberglass reinforced polyester wetted elbow, a packed tower caustic scrubber, and an induced draft fan (Carnes, 1984; Ross, et al., 1986; Ross, et al., 1984).

A total of four trial burns were performed in 1985 between September 4th and September 21st. These included a blank burn to establish background emission levels, a short-duration (4 hrs.) burn to establish feed capabilities and to test the sampling protocol, and two full waste burns (10 hr. duration) to establish the DREs for dioxin (Ross, et al., 1986).

The results of the two full waste burns are presented in Table 4.1.1. The data show that the 2,3,7,8-TCDD DRE was greater than 99.9997 percent as measured in the virtual stack (E-DUCT) which would correspond to the stack of an actual hazardous waste incinerator. The reason six nines DRE could not be established was that the detection limits experienced in the sampling and analysis protocols used were not sufficiently low (Ross, et al., 1986; Carnes, 1986). Despite this, it was concluded from the data in the study that "incineration under the conditions existing in the CFR pilot incineration system for these tests is capable of achieving 99.9999 percent dioxin DRE" (Ross, et al., 1986). It was further concluded that land-based incineration should be considered a viable disposal method for the Vertac still bottoms waste given that appropriate safeguards are employed (Ross, R. W., et al., 1986).

The concentrations of 2,3,7,8-TCDD and other CDDs and CDFs were also measured in the scrubber blowdown water and kiln ash (Ross, et al., 1986). The maximum concentration of 2,3,7,8-TCDD detected in the scrubber blowdown was 0.12 picograms per milliliter (approximately 0.1 ppt). In most samples of blowdown, all forms of CDDs were undetected at detection limits of 0.006 to 0.020 pg/ml. In one sample, however, 0.78 pg/ml of Octa-CDD was detected. No 2,3,7,8-TCDF was detected in any blowdown samples. Total TCDF was detected at 0.20 pg/ml in all 4 samples. Tetra-, penta-, hexa- and hepta- CDD and CDFs were not detected in any of the kiln ash samples at detection limits ranging from 1.3 to 37 picograms per gram (ppt).

Since in all cases the residues from this incinerator contained CDDs and CDFs at levels below 1 ppb, it would be expected that these residues could be land disposed in accordance with the screening levels proposed in 51 FR 1602. These screening levels are based on the use of a different analytical method (Method 8280) than used in the present situation. Therefore, definite conclusions cannot be made. Nonetheless, the concentrations of CDDs and CDFs detected in the treatment residues indicate that a high degree of destruction did occur.

Several problems encountered during the trial burns should be mentioned. These include (Ross, et al., 1986):

1. Waste was fed into the kiln through a water-cooled feed lance using a Moyno cavitation pump. The lance frequently became clogged due to carbon-buildup from coking of the waste material.
2. The test plan called for continuous monitoring of flue gas, CO₂, O₂, CO and NO_x, at the stack with one set of emission analyzers and at the kiln exit and afterburner exit on a time-share basis with another set. However, only one set of emission analyses was operational during most of the test series. Therefore, no kiln emission monitoring data were obtained. Very little simultaneous afterburner exit and stack data were obtained.
3. An air leak in the sample transfer line from the afterburner exit to the monitors caused the data to be "substantially compromised". Also, difficulties were encountered while monitoring by means of the isokinetic Method 5 sampling train (MM5). The glass frit in the MM5 train condensor/XAD2 sorbent cartridge frequently became plugged. Most exhaust and stack sampling was at less than 50 percent isokinetic, which compromises the particulate emission results.

4.1.3 Costs of Treatment

Currently, there are no stationary kilns permitted to burn dioxin wastes. Thus, no costs are available. However, these costs would be expected to be similar to or greater than the costs for PCBs incineration. Table 4.1.2 lists the average unit costs for PCBs wastes at the currently permitted stationary rotary kiln facilities.

4.1.4 Process Status

Land-based incineration systems with potential to treat dioxin wastes include commercial incineration facilities which have been approved for PCB disposal, in addition to RCRA hazardous wastes. These incinerators are operated by Rollins Environmental Services (Deer Park, Texas), ENSCO (El Dorado, Arkansas) and SCA (Chicago, Illinois). Each of these systems contains a rotary kiln incinerator followed by an afterburner section which can also be used independently as a liquid injection incinerator.

The Rollins and ENSCO facilities can accept both liquid and solid wastes, but the SCA incinerator has only been approved for the disposal of liquid PCB wastes. The following are the maximum feed rates for these land-based incineration systems (GCA, 1985; Clarke, 1986):

Rollins (Deer Park, TX).	1,440 lb/hr for solids 6,600 lb/hr for liquids
ENSCO (El Dorado, AK.)	2,500 lb/hr for solids 5,000 lb/hr for liquids
SCA (Chicago, IL.)	2,910 lbs/hr for solids 6,300 lbs/hr for liquids

Although none of these facilities has conducted trial burns for the destruction of dioxin-contaminated waste, their ability to demonstrate six nines DRE for PCBs suggests that they would be able to destroy dioxins. Results of trial burns using the CRF pilot-scale rotary kiln incinerator show the potential for dioxin destruction at the RCRA regulated DRE.

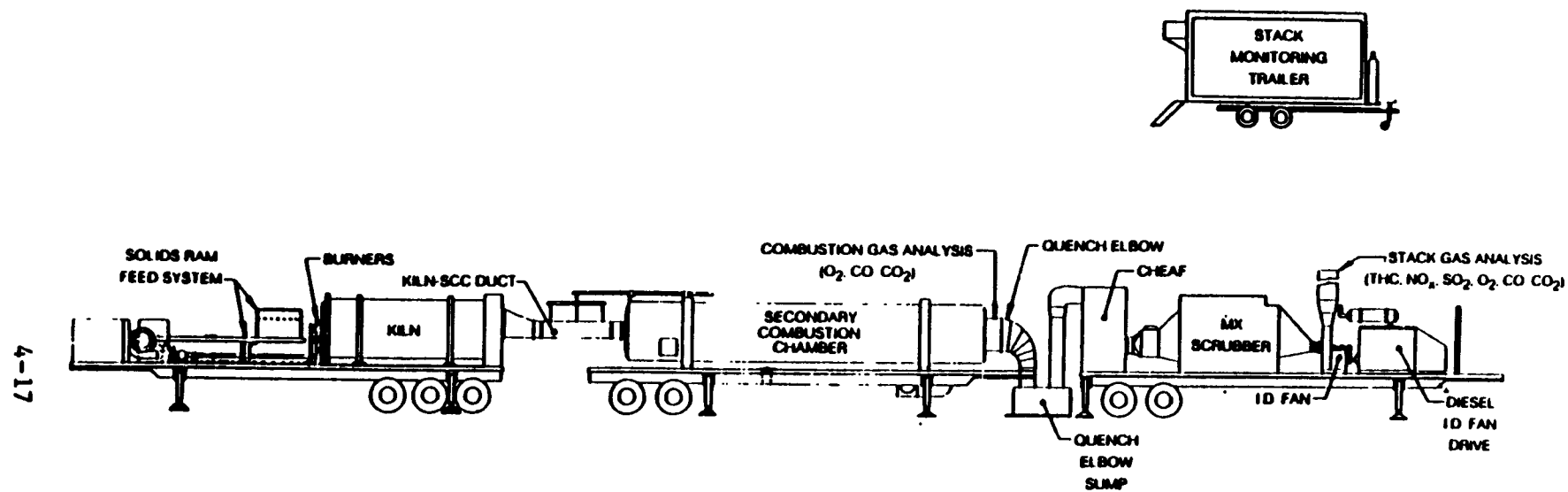


Figure 4.2.1. Schematic of EPA mobile incineration system [U.S. EPA, 1984].

Figure 4.2.2. Schematic flow diagram of ENSCO MWP-2000 Mobile Rotary Kiln Incinerator [Pyrotech Systems, 1985].

Operating Parameters--

Operating parameters for the two mobile rotary kiln systems are summarized below (U. S. EPA, 1984; Sickels, 1986; Freestone, et al., 1985):

Waste Forms	EPA/MIS	ENSCO
	Solids, Liquids	Solids, Liquids
Maximum Waste Feed Rate (lb/hr)		
-Solids to Rotary Kiln	9,000	10,000
-Liquids to Rotary Kiln		3,000
-Liquids to SCC	1,500	4,000
Kiln Temperature (°F)	1800	1800
SCC Temperature (°F)	2200	2200
SCC Residence Time (sec)	2.2	2

Severe weather conditions can effect the operation of the mobile incinerator. For instance, extremely cold weather during the initial stages of the EPA Mobile incinerator trial burns on the Denney Farm site caused the No. 2 diesel fuel to gel, hydraulic fluids to thicken, and water lines to freeze (IT Corporation, 1985a; Krogh, 1985).

4.2.2 Technology Performance Evaluation

Initial trial burns with the EPA mobile incinerator were conducted in Edison, New Jersey using surrogate compounds to mimic RCRA-listed constituents such as dichlorobenzene, trichlorobenzene, tetrachlorobenzene, and PCBs. In these liquid waste trial burns, up to six nines DRE of PCBs was demonstrated. Following this, laboratory studies were conducted to establish optimum conditions for treating soils contaminated with dioxin. The following conclusions were made based on these studies (IT Corporation, 1985a):

- Thermal treatment of contaminated Missouri soils was capable of achieving 1 ppb or lower concentration of residual 2,3,7,8-TCDD and other chlorinated dioxins and chlorinated furans in the incinerator ash.

TABLE 4.2.1. SOILS USED IN THE EPA MOBILE INCINERATOR DURING
PRELIMINARY TESTING OF THE SOLIDS FEED SYSTEM

Soil type	Test purpose	Particulate emissions
Denney Farm Area Soil	To ensure that there were no unusual problems with soil from that area; Site soil was very dry from being stored	18 mg/Nm ³
Montmorillonite	Planned to be used as the Solids Carrier in Test 1 of Solids Trial Burn	17 mg/Nm ³
Coral from Florida	Potential Future Use of EPA/MIS for U.S. Air Force on Johnston Island Contaminated Coral	9 mg/Nm ³
Clarksburg (New Jersey) Soil	Readily Available Soil in the Missouri Area	Not Available

Reference: IT Corporation, 1985a.

TABLE 4.2.3. MISSOURI DEPARTMENT OF NATURAL RESOURCES AND EPA DELISTING
PARAMETERS FOR ORGANIC CONSTITUENTS IN INCINERATOR ASH
AND SCRUBBER WASH WATER

<u>Toxic Constituent</u>	<u>Concentration</u>	
	<u>Ash</u>	<u>Scrubber water</u>
Dioxins/Dibenzofurans ^a	1 ppb	10 ppt
2,3,4-Trichlorophenol	100 ppm	10 ppm
2,3,5-Trichlorophenol	100 ppm	10 ppm
2,4,6-Trichlorophenol	1 ppm	50 ppb
2,5-Dichlorophenol	350 ppb	15 ppb
3,4-Dichlorophenol	100 ppm	10 ppm
2,3,4,5-Tetrachlorophenol	1 ppm	50 ppb
2,3,4,6-Tetrachlorophenol	1 ppm	50 ppb
1,2,4,5-Tetrachlorobenzene	100 ppm	10 ppm
1,2,3,5-Tetrachlorobenzene	100 ppm	10 ppm
Hexachlorophene	200 ppm	5 ppm
Polychlorinated Biphenyls	2 ppm	1 ppm
Benzo(a)pyrene	5 ppm	10 ppb
Benzo(a)anthracene	5 ppm	10 ppb
Chrysene	50 ppm	1 ppm
Dibenzo(a,h)anthracene	5 ppm	10 ppb
Indeno(1,2,3-c,d)pyrene	5 ppm	10 ppb
Benzo(b)fluoranthene	5 ppm	10 ppb

^aWeighted average of TCDDs/TCDFs, PeDDs/PeDFs, and HxCDDs/HxCDFs using toxicity weighting factors.

Reference: Poppiti, 1985; U.S. EPA, 1985.

Average operating parameters during the trial burn for dioxin-contaminated soil and liquids were as follows (IT Corporation, 1985 a and b; U. S. EPA, 1985):

Kiln Temperature	1800°F
SCC Temperature	2200°F
SCC Combustion Gas Flow Rate	13,500 acfm
SCC Residence Time	2.6 seconds
Waste Feed Rate	2000 lb/hr (soil) 250 lb/hr (liquid)
Auxiliary Fuel	
-Kiln	5 to 6 million Btu/hr
-SCC	4 to 5 million Btu/hr

Following the successful (demonstrating 99.9999 percent DRE) completion of these preliminary trial burns, additional test burns were planned for the EPA/MIS as summarized in Table 4.2.4. As noted in the table, burns of the material from five of these sites (Denney Farm, Neosho, Erwin Farm, and Talley Farm) have been completed. The total amount of dioxin-contaminated material that was successfully burned (i.e., achieved greater than six nines DRE) included 2 million pounds of soils and 180,000 pounds of liquids (Hazel, 1986; Freestone, 1986). The material from the remaining sites listed in Table 4.2.4 is scheduled to be burned as soon as funding becomes available (Hazel, 1986). Currently, the amount of dioxin-contaminated material that remains to be burned includes 600,000 pounds of soil and 80,000 pounds of liquid wastes (Hazel, 1986).

During the incineration of the dioxin-contaminated wastes from these sites, several parameters were monitored continuously, including: CO, CO₂, O₂, NO_x, operating temperatures and feed rates (Hazel, 1986; Freestone, 1986). Built-in safety controls cause the operations to stop if any of these parameters are not within the proper range (Hazel, 1986). In addition, the waste residues from the burns (i.e., ash and water) are continually monitored. To date, dioxin has never been found in the burn residues (Hazel, 1986). More detailed data will be available in the Final Report scheduled for release within the next few months (Freestone, 1986).

TABLE 4.2.5. EMISSION DATA FOR THE ENSCO MOBILE INCINERATOR (MWP-75)
PCB TRIAL BURN

Condition	Result
PCB DRE	>99.9999%
Carbon Monoxide	20 ppm
Nitrogen Oxides	300 to 500 ppm
Particulate	Met or exceeded all standards
HCl Scrubbing	99% at 1,500 lb HCl/hr

Reference: Sickels, 1986; Pyrotech Systems, 1985.

Initially, ENSCO encountered slagging problems which were solved by adding six chutes to the secondary unit and a cyclone was installed prior to the secondary unit to remove fine particulates (Pyrotech Systems, 1985). These modifications increase the treatment costs.

One of the MWP-2000 units is currently located at a site near Tampa, Florida where it is being used to clean up a site containing liquids contaminated with chlorinated organics (McCormick, 1986; Lee, 1985). A second MWP-2000 unit located at the El Dorado, Arkansas facility (i.e., the location of the ENSCO stationary rotary kiln system) has just completed a series of dioxin trial burns using wastes from the Vertac Site. The results are expected to be released in May 1986 (McCormick, 1986). The construction of the third MWP-2000, a computer-operated unit, is not complete yet. Upon completion, this third unit is scheduled to undergo tests by the Air Force to handle dioxin-contaminated coral at Johnston Island (Lee, 1985; McCormick, 1986).

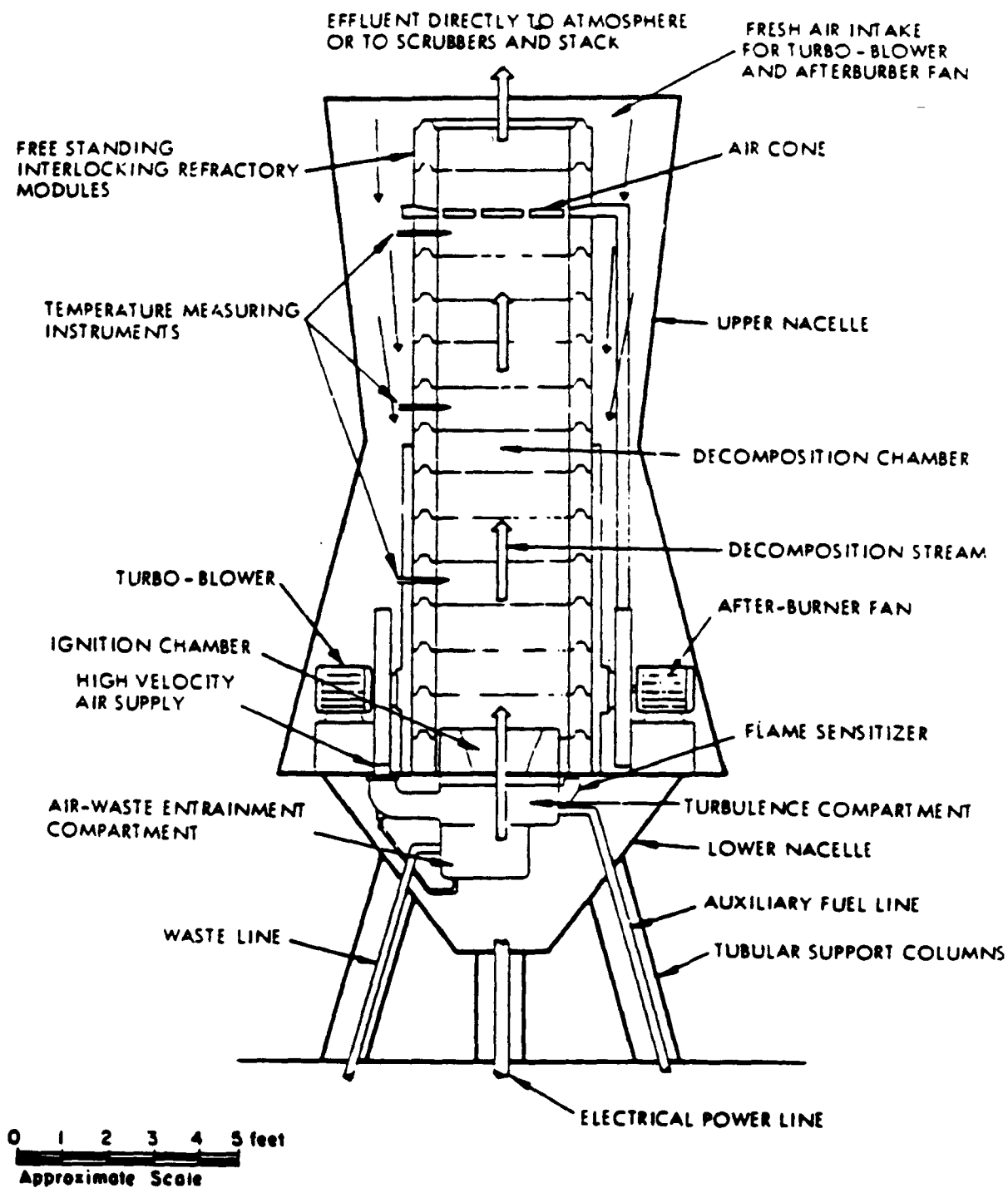


Figure 4.3.1. Vertically-oriented Liquid Injection Incinerator
[Bonner, 1981].

Operating Parameters--

Typical operating parameters for the vertically-configured LI incinerator on the Vulcanus are as follows (U. S. EPA, 1983; U. S. EPA, 1978):

Residence Time	0.5 to 2.0 seconds
Temperature	650 to 1750°C (1200 to 3180°F)
Air Feed Rate	65,000 to 75,000 m ³ /hr
Waste Feed Rate Capacity	7 to 10 tons/hr

4.3.2 Technology Performance Evaluation

The only documented burns of waste containing dioxins in a liquid injection incinerator are those that took place on board incinerator ships. These burns took place between July and September 1977. Three shiploads (totalling approximately 10,400 metric tons) of U.S. Air Force stocks of Herbicide Orange were incinerated by the M/T Vulcanus in the Pacific Ocean west of Johnston Atoll (U. S. EPA, 1978). A summary of the DREs achieved in these burns and other U.S.-sponsored ocean burns is presented in Table 4.3.1. Operating parameters for these Herbicide Orange trial burns are summarized in Table 4.3.2.

The Herbicide Orange stock consisted of an approximately 50-50 volume mixture of the n-butyl esters of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) (U. S. EPA, 1978). A small quantity of the stock contained a 50-50 volume mixture of 2,4-D and the iso-octyl ester of 2,4,5-T. Certain lots also contained 2,3,7,8-TCDD ranging in concentration from 0 to 47 ppm (with an average concentration of 1.9 ppm). Drums containing the waste stock and waste handling equipment were rinsed with diesel fuel which was subsequently mixed with the waste feed to increase its heating value for incineration (U. S. EPA, 1978).

TABLE 4.3.2. SUMMARY OF OPERATING PARAMETERS FOR
HERBICIDE ORANGE TRIAL BURNS USING LIQUID
INJECTION INCINERATION ON THE VULCANUS

Flame Temperature	1375-1610°C
Furnace Wall Temp.	1100-1200°C
Residence Time	1.0 to 2.0 seconds

Reference: U. S. EPA, 1978

During the period from December 1981 through January 1982, the first ocean burn of PCBs was performed in U.S. waters (U. S. EPA, 1983). A second shipload of PCB-containing wastes were incinerated aboard the M/T Vulcanus during August 15-31, 1982 (U. S. EPA, 1983). Operating parameters for the PCBs burns are summarized in Table 4.3.3. An EPA-sponsored test project was performed during the second PCBs trial burn to measure emissions of polychlorinated biphenyls (PCBs), chlorobenzenes (CBs), tetrachlorodibenzofurans (TCDFs), and tetrachlorodibenzo-p-dioxins (TCDDs).

TABLE 4.3.3 SUMMARY OF OPERATING PARAMETERS FOR
PCB TRIAL BURNS USING LIQUID INJECTION
INCINERATION ON THE VULCANUS

Flame Temperature	1648-2048°C
Furnace Wall Temp.	1281-1312°C
Residence Time	1.1 to 1.5 seconds
Feed Rate	5.23-6.79 mt/hr

Reference: U. S. EPA, 1983.

No TCDDs were detected in any sample of waste or stack gas during the tests. Detection limits for the waste ranged from less than 2 ppb to less than 22 ppb. TCDFs, however, were detected in the waste feed at ppb levels and in the stack gas at low ppt levels. [USEPA, 1983]

TABLE 4.3.4. SUMMARY OF LIQUID INJECTION INCINERATION TRIAL BURN
RESULTS FOR PCBs - GENERAL ELECTRIC, PITTSFIELD, MA

Parameter	Trial burn results
Temperature Inside the Reactor Chamber	1,262°C - 1,141°C (2,303°F - 2,085°F)
Residence (Dwell) Time of Combustion Products	4.02 sec
Combustion Efficiency	99.993%
Oxygen Concentration during PCB Incineration	9.5 - 10.5%
Waste Oil Firing Rate	1.09 - 119 GPM
PCB Concentration in Oil	18.4 - 20.0%
Average PCB Destruction Efficiency	99.999982%
Average PCB Destruction and Removal Efficiency	99.999982%
HCl Scrubber Efficiency	99.82%
Particulate Emissions @ 12% CO ₂	0.543 lb/hr 0.0361 gr/dscf
NO _x Emissions	18.3 ppm 0.43 lb/hr
RCI Emissions	0.000304 ppm 0.00002542 lb/hr
HCl Emissions	0.2752 lb/hr

Reference: Thayer, et al., 1983.

4.4 FLUIDIZED BED/CIRCULATING FLUIDIZED BED (CFB) SYSTEM

4.4.1 Process Description

The fluidized bed incinerator uses high temperature oxidation under controlled conditions to destroy organic constituents in liquid, gaseous, and solid waste streams. It is typically used for slurries and sludges.

As shown in Figure 4.4.1, a typical fluidized bed incinerator consists of a vertical refractory-lined cylindrical vessel containing a bed of inert granular material (typically, sand) on a perforated metal plate. The waste (in the form of either gas, liquid, slurry, or sludge) is usually injected into or just above the stationary bed. The granular bed particles are fluidized by blowing air upward through the medium. The resulting agitation ensures intimate mixing of all waste material with combustion air (McGaughey, et al., 1984; Bonner, 1981).

A burner located above the bed is used to heat the bed to start-up temperature. The large mass and high heat content of the bed causes the waste to rapidly combust which, in turn, transfers heat back to the bed. The maximum temperature of the granular bed is limited by the softening point of the bed material (for sand this temperature is 1100°F). The residence time of waste material in the bed typically ranges from 12 to 14 seconds for liquid wastes. The solid uncombustible materials in the waste become finely suspended particulate matter which is separated in a cyclone while the exhaust gases pass through an afterburner to destroy vapor-phase residuals (McGaughey, et al., 1984; Bonner, 1981).

Waste Tech Services, Inc. has developed a Low-Temperature Fluidized Bed that functions similarly to the conventional fluidized bed except that a higher air volume is forced through the bed material (Rasmussen, 1986; Freeman, 1985). Also, the bed is composed of a mixture of a granular combustion catalyst and limestone. Limestone is continuously added to the bed and the bed material is periodically drained from the vessel. A multicyclone system employing a baghouse to clean the flue gas is used for air-pollution control. The Waste-Tech fluidized bed is able to operate at lower temperatures than conventional fluidized beds and also has reduced supplemental fuel requirements (Rasmussen, 1986; Freeman, 1985).

Another modification of the conventional fluidized bed technique that has been developed is the Circulating Fluidized Bed Combuster (Figure 4.4.2). It utilizes contaminated soil as the bed material and air flow rates 3 to 5 times greater than conventional systems (Rickman, et al., 1985; Vrable, et al., 1985a and b; Barner, 1985). The high air flow causes increased turbulence which allows for efficient combustion at much lower operating temperatures without requiring the use of an afterburner. A comparison of the circulating fluidized bed combustor with the conventional fluidized bed is shown in Table 4.4.1.

The startup combustor burner consists of a natural gas fuel system (Rickman, et al., 1985; Vrable, et al., 1985a and b; Barner, 1985). It has a 4 to 6 hour cold startup period, and an approximately 30 minute hot restart (with a refractory temperature at or greater than 1400°F). The startup burner is generally idle during waste burning unless the waste feed is interrupted and it is required to maintain a low combustor temperature. The combustor is a carbon-steel tube with refractory lining which consists of an erosion-resistant inner layer and a thermal insulating outer layer. Prior to being injected into the combustion chamber the waste feed is mixed with hot recirculating solids from the cyclone. Both the waste feed and the recirculated solids are introduced into the combustion chamber. Liquid and slurry waters are pumped from stirred tanks whereas a metering screw is used to convey solids and sludges.

The combustor has primary and secondary air ports through which fluidizing air is provided by a constant-speed, motor-driven forced-draft fan (GA Technologies, 1985; Rickman, et al., 1985). The high air velocity (15 to 20 feet/second) entrains both the bed and the combustible waste which rise through the reaction zone to the top of the combustion chamber and pass into a hot cyclone.

The cyclone is constructed of carbon-steel and lined with castable refractory lining. The function of the cyclone is to separate bed material from the combustion gases and recirculate these solids to the combustion chamber. The hot combustion gases flow to an off-gas heat exchanger where they are cooled to 375°F and then directed to baghouse filters to remove any residual products of incomplete combustion (GA Technologies, 1985; Rickman, et al., 1985).

TABLE 4.4.1. COMPARISON OF CONVENTIONAL FLUIDIZED BED WITH
CIRCULATING FLUIDIZED BED COMBUSTOR

Condition	Circulating fluidized bed	Conventional fluidized bed
<u>Feeding</u>		
No. of Inlets	1-solid; 1-liquid	5-solid; 5-liquid
Sludge Feeding	Direct	Filter/Atomizer
Solids Feed-size	<1 in.	<0.5-0.25 in.
<u>Pollution Control</u>		
POHCs	In moderate temp. combustor	In high temp. combustor or afterburner
Cl,S,P	Dry limestone in combustor	Downstream scrubber
Upset Response	Slump bed; no release	Bypass scrubber pollution release
Effluent	Dry Ash	Wet Ash Sludge
<u>Efficiency</u>		
Thermal	>78%	>75%
Carbon	>98%	>90%

Reference: Rickman, et al., 1985

4.4.2 Technology Performance Evaluation

Fluidized beds have been used to treat municipal wastewater treatment plant sludges, oil refinery waste, pulp and paper mill waste, pharmaceutical wastes, phenolic wastes, and methyl methacrylate. Pilot-scale demonstrations have been performed for other hazardous wastes. Currently, there are more than 25 circulating bed combustors operating in the U.S. and Europe. However, there are currently no units operating commercially as hazardous waste incinerators (Freeman, 1985; Rickman, et al., 1985).

The low-temperature fluidized bed combustor (designed by Waste Tech Services, Incorporated) was used to conduct trial burns on soil contaminated with carbon tetrachloride and dichloroethane (Freeman, 1985). Only four nines DRE was demonstrated. The results of these tests are summarized in Table 4.4.2.

GA Technologies has conducted trial burns on its pilot scale circulating bed combustor using chlorinated organic liquid wastes. The combustor was operated at 1540 to 1600°F with a gas velocity of 11 to 12 feet/second and 45 to 60 percent excess air. Limestone was injected into the incinerator with the liquid waste feed to prevent the formation of HCl by capturing the chlorides formed. The following results were obtained (Rickman, et al., 1985; Chang and Sorbo, 1985):

NO _x emissions	40 ppm (average)
SO ₂ emissions	250 to 350 ppm
CO emissions	1000 ppm
Chloride Capture	99%
Flue Gas Emissions (%-DRE)	
- Ethylbenzene	>99.99
- 1,1,2-trichloroethane	>99.99
- 1,2-dichloroethane	>99.99
- 1,1-dichloroethylene	>99.99
- 1,2-transdichloroethylene	>99.99
- vinyl chloride	>99.99
- toluene	>99.99
- benzene	>99.99

The pilot-scale unit was also used to conduct trial burns on PCB-contaminated soil (Rickman, et al., 1985; Chang and Sorbo, 1985). An auxilliary fuel was used to maintain bed temperature at 1600 to 1800°F. A destruction efficiency exceeding six nines (99.9999 percent) was achieved. A summary of the test conditions and results is given in Table 4.4.3.

4.4.3. Costs of Treatment

The costs for the conventional fluidized bed are dependent on fuel requirements, scale, and site conditions. However, the costs are generally comparable with conventional rotary kiln incineration technology. Waste-Tech Services, Inc. lists the costs in Table 4.4.4 as being typical for their low-temperature fluidized bed (Freeman, 1985).

Costs for the circulating bed combustor vary according to the size of the incineration unit, and the type of waste being processed. Estimated costs for a 25 million Btu/hr unit are given in the Table 4.4.5 (Freeman, 1985):

4.4.4 Process Status

Currently, there are several fluidized bed combustors operating worldwide. Although fluidized beds have been used in various industries, at the present time there are not any fluidized beds operating commercially as hazardous waste incinerators. However, the fluidized bed, particularly the circulating fluidized bed, appear to have significant potential for future use in the destruction of hazardous wastes.

The low-temperature fluidized bed developed by Waste Tech Services requires additional testing and/or development, but could potentially be used for the destruction of dioxin contaminated wastes.

A stationary pilot scale circulating fluidized bed unit capable of incinerating a ton per hour of hazardous waste is in operation at the GA Technologies test facility. A transportable incinerator has also been constructed for use in onsite demonstrations on PCBs contaminated wastes. Although dioxin trial burns have not been conducted, GA Technologies would be interested in performing dioxin testing if funding were available (Jensen, 1986).

TABLE 4.4.4. WASTE-TECH FLUIDIZED BED COSTS

Item	Cost
Operating Labor	0.0084 \$/lb
Consumables and Utilities	0.0138 \$/lb
Nonlabor (capital depreciation, siting cost, maintenance mat'ls, insurance, tax overhead)	0.0116 \$/lb
Limestone for Chlorine Removal, Waste Excavation, Ash Disposal, etc.	<u>0.043 \$/lb</u>
TOTAL COST	\$150/ton

Note: These cost estimates are for a 50 sq.ft. system with a throughput of 9,200 lb/hr for soils having 2 percent organics and 5 percent moisture content.

TABLE 4.4.5. CIRCULATING FLUIDIZED BED COSTS

Feed Type	Installed Capital Costs	Annual Operating Costs	Total Cost per Unit of Feed
Chlorinated Organic Sludge	\$2.0 million	\$0.25 million	\$60/ton
Contaminated Soil	\$1.8 million	\$0.35 million	\$27/ton
Wet Sludge	\$1.8 million	\$0.35 million	\$32/ton

Note: Costs are based on the use of a 25 million Btu/hr unit.

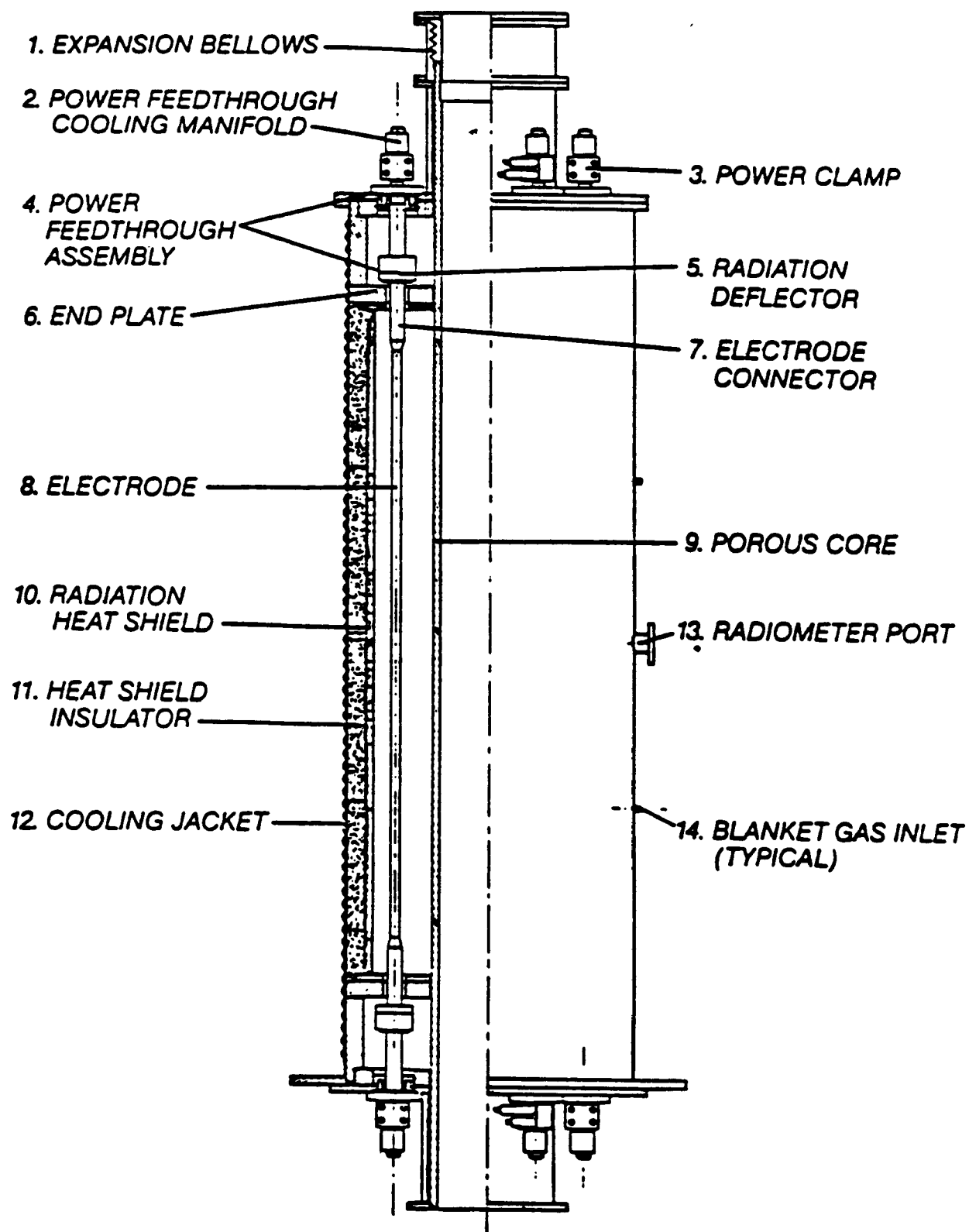


Figure 4.5.1. Advanced Electric Reactor [Huber].

residence time (5 seconds). The second postreactor treatment zone is water-cooled, and its primary purpose is to cool the gas prior to downstream particulate cleanup.

Off gas cleaning equipment includes a cyclone to collect particles which do not fall into the solids bin, a bag filter to remove fines, an aqueous caustic scrubber for acid gas and free chlorine removal, and two banks of five parallel activated carbon beds in series for removal of trace residual organics and chlorine.

The stationary pilot scale reactor which has been used for testing various wastes at their Borger, Texas facility consists of a porous graphite tube, 1 foot in diameter and 12 feet high, enclosed in a hollow cylinder with a double wall cooling jacket. This pilot unit is capable of processing 5000 tons/yr of waste. Huber also has a 3 inch diameter mobile unit which has been transported to hazardous waste sites for testing purposes. Test results are described below.

Restrictive Waste Characteristics--

The AER cannot currently handle two-phase materials (i.e., sludge); it can only burn single-phase materials consisting of solids, or liquids, or gases alone (Schofield, 1985; Boyd, 1986). Generally, a solid feed must be free flowing, nonagglomerating, and smaller than 100 mesh (less than 149 micrometers or 0.0059 inches) (GCA, 1985; Shofield, 1985). However, depending on the required destruction, solids larger than 100 mesh (but smaller than 10 mesh) may be suitable. Soils should be dried and sized before being fed into the reactor.

Also, the Huber process is not cost competitive with standard thermal destruction techniques (such as the rotary kiln) for materials with a high Btu content (Schofield, 1985; Boyd, 1986). It is cost-effective for wastes with a low Btu content (i.e., PCBs and dioxin) because unlike standard thermal destruction techniques, the Huber process does not require supplementary fuels to obtain the necessary Btu content for incineration.

TABLE 4.5.1. SUMMARY OF OPERATING PARAMETERS AND RESULTS
FOR HUBER AER RESEARCH/TRIAL BURNS

Condition	PCBs (Sept. 1983)	CCl ₄ (May 1984)	Dioxins (Oct/Nov 1984)
Reactor Core Temperature (F)	4100	3746-4418	3500-4000
Waste Feed Rate (lb/min)	15.5-15.8	1.1-40.8	0.4-0.6
Nitrogen Feed Rate (scfm)	147.2	104.3-190.0	6-10
Z-DRE	>99.99999	>99.9999	>99.999

Reference: Schofield, 1984; Roy F. Weston, 1985.

4.5.3 Costs of Treatment

Operating costs will vary depending on the quantity of material to be processed and the characteristics of the waste feed (Lee, et al., 1984). Pretreatment may be necessary for bulky wastes having a high moisture content. Typical energy requirements for normal soil range from 800 to 1000 kwh/ton.

Cost estimates for processing a site containing more than 100,000 tons of waste material were approximately \$365 to \$565/ton in 1985 (Lee, et al., 1984; Freeman and Olexsey, 1986). The cost breakdown for this estimate was 12 percent for maintenance, 7 percent labor, 29 percent energy, 18 percent depreciation and 34 percent for other costs (permitting, setup, post-treatment, etc.). These costs have recently been updated. The new costs are expected to be released in May 1986 (Boyd, 1986).

4.5.4 Process Status

The J.M. Huber Corporation purchased the patent rights from Thagard Research Corporation. Huber then modified the design of the reactor (primarily the feed tube and the core design) to improve the efficiency of the reactor, extend the lifetime of the electrodes and core material, and to reduce sticking of vitreous material on the core walls (which lowers efficiency) (Boyd, et al., 1986).

Huber maintains two fully-equipped reactors at their pilot facility in Borger, Texas (Schofield, et al., 1985). The smaller reactor, which is equipped for mobile operation, has a 3-inch core diameter and a capacity of 0.5 lb/min.. The larger reactor is commercial scale with a 12-inch core diameter and a capacity of 50 lb/min. Both of these reactors are used primarily for research purposes. In May 1984, the Huber reactor was certified by the EPA under TSCA to burn PCB wastes. Recently, the U.S. EPA and the Texas Water Commission jointly issued J.M. Huber Corporation a RCRA permit which authorizes the incineration of any non-nuclear RCRA hazardous waste (including dioxin-containing wastes) in the Huber Advanced Electric Reactor (AER)(HMIR, 1986). This was the first commercial permit issued under

4.6 INFRARED DESTRUCTION (Shirco)

4.6.1 Process Description (Daily, 1986; Shirco, 1985; Freeman and Olexsey, 1986; HMIR, 1986; Technical Resources Inc., 1985; Daily, 1985)

Shirco Infrared Systems, Inc. has developed a portable infrared incineration system, which can be transported in a 45 ft trailer. The major components of the system include a feed metering system, an infrared primary chamber furnace, a combination propane-fired/infrared secondary chamber, a venturi scrubber system, blower and heating control systems, and a monitoring and control system.

The waste material is fed by bucket or inclined conveyor onto a metering conveyor which controls the amount and rate of waste feed into the primary furnace. The primary furnace chamber is constructed of carbon steel, lined with multiple layers of ceramic fiber blanket-insulation mounted on stainless steel studs and retained with ceramic fasteners. The external dimensions of the primary chamber are 2.5 ft x 9 ft x 7 ft, and it weighs (installed) 3,000 lbs. Infrared heating elements, consisting of silicon carbide rods with external electrical connections at each end, are spaced along the length of the furnace. The chamber can be heated to temperatures ranging from 500 to 1,050°C. Residence times for the feed material are variable ranging between 10 and 180 minutes. The temperatures and times will depend on the characteristics of the waste.

Following combustion, the ash (or processed material) is conveyed to the end of the furnace where it drops off the belt and passes through a chute into an enclosed, tapered hopper. A discharge screw conveyor controls transport of the discharged material from the hopper into sealed collection drums.

Combustion air is forced through a combustion air preheater and then injected at 10 points along the length of the primary chamber furnace. Depending on the waste characteristics, the exhaust gases may be directed to a secondary combustion chamber to complete gas-phase combustion reactions.

The secondary chamber is a rectangular carbon steel box lined with a ceramic fiber blanket insulation. The secondary chamber weighs 1,500 lbs and has external dimensions of 3 ft x 9 ft x 3 ft. Combustibles in the gas are ignited via a propane-fired burner and are maintained at a predetermined setpoint temperature using an array of silicon carbide heating elements which

TABLE 4.6.1 OPERATING PARAMETERS AND RESULTS FOR SHIRCO INFRARED
DESTRUCTION PILOT TESTS

Condition	Test 1	Test2
TCDD in Feed (ng/g)	227	156
Solid Phase Residence Time (min)	30	15
Solid Feed Rate (lb/hr)	47.68	48.12
Primary Chamber Temp.-Zone A (°F)	1560	1490
Primary Chamber Temp.-Zone B (°F)	1550	1490
Secondary Chamber Temperature (°F)	2250	2235
Emissions Sampling Duration (hours)	7	2.5
Particulate at 7% O ₂ (gr/dscf)	0.0010	0.0002
Gas Phase DRE of 2,3,7,8,-TCDD at Detection Limit (picograms)	>99.999996 14	>99.999989 8.4
Ash Analysis for 2,3,7,8-TCDD at Detection Limit (ppt)	ND 38	ND 33

Reference: ERT, 1985; Daily, 1986.

4.7 PLASMA ARC PYROLYSIS

4.7.1 Process Description

Operation and Theory--

In this process waste molecules are destroyed by the action of a thermal plasma field. The field is generated by passing an electrical charge through a low pressure air stream, thereby ionizing the gas molecules and generating temperatures up to 10,000°C.

A flow diagram of the plasma pyrolysis system is shown in Figure 4.7.1. The plasma device is horizontally mounted in a refractory-lined pyrolysis chamber with a length of approximately 2 meters and a diameter of 1 meter. Liquid wastes are injected through the colinear electrodes of the plasma device where the waste molecules dissociate into their atomic elements. These elements then enter the pyrolysis chamber which serves as a mixing zone where the atoms recombine to form hydrogen, carbon monoxide, hydrogen chloride and particulate carbon. The approximate residence times in the atomization zone and the recombination zone are 500 microseconds and 1 second, respectively. The temperature in the recombination zone is normally maintained at 900-1,200°C (Barton, 1984).

After the pyrolysis chamber, the product gases are scrubbed with water and caustic soda to remove hydrochloric acid and particulate matter. The remaining gases, a high percentage of which are combustible, are drawn by an induction fan to the flare stack where they are electrically ignited. In the event of a power failure, the product gases are vectored through an activated carbon filter to remove any undestroyed toxic material.

The treatment system that is currently being used for testing purposes is rated at 4 kg/minute of waste feed or approximately 55 gal/hour. The product gas production rates are 5-6 m³/minute prior to flaring. To facilitate testing, a flare containment chamber and 30 ft stack have also been added to the system. The gas flow rate at the stack exit is approximately 36 m³/minute (Kolak, Barton, Lee, Peduto, 1986).

A major advantage of this system is that it can be moved from waste site to waste site as desired. The entire treatment system, including a laboratory, process control and monitoring equipment, and transformer and switching equipment, are contained on a 45 ft tractor-trailer bed (Barton, 1984).

Two residual streams are generated by this process. These are the exhaust gases released up the stack as a flare, and the scrubber water stream. Since the product gas (after scrubbing) is mainly hydrogen, carbon monoxide, and nitrogen, it burns with a clean flame after being ignited. Analysis of the flare exhaust gases, presented in the following section, indicates virtually complete destruction of toxic constituents.

The scrubber water stream is composed mainly of salt water from neutralization of HCl and particulates, primarily carbon. Analyses of the scrubber water for the waste constituent of concern (e.g., carbon tetrachloride (CCl_4) and PCB in the feed material) have shown that the constituents were present at low ppb concentrations. The quality of scrubber water generated would depend on the water feed rate and corresponding product gas and scrubber waste flowrates. During a test in which 2.5 kg/min of waste containing 35 to 40 percent CCl_4 was fed to the reactor, a scrubber water effluent flowrate of 30 l/minute was generated (Kolak, Barton, Lee, Peduto, 1986).

Restrictive Waste Characteristics--

The reactor as it is currently designed can only be used to treat liquid waste streams with viscosities up to that of 30 to 40 weight motor oils. Particulates are removed by a 200 mesh screen prior to being fed into the reactor. Contaminated soils and viscous sludges cannot be treated. The TCDD wastes for which this technology has potential include nonaqueous phase leachate such as that which has been generated at the Love Canal and Hyde Park Landfills, unused liquid herbicide solutions such as herbicide orange, and possibly still bottoms from herbicide production.

4.7.2 Technology Performance Evaluation

The plasma arc system has been tested using several liquid feed materials including carbon tetrachloride (CCl_4), polychlorinated biphenyls (PCBs), and methyl ethyl ketone (MEK). It has not been tested on wastes or other materials contaminated with TCDD. However, because of the structural similarity between TCDD and PCBs, the data presented should provide some indication as to the potential of this technology towards destroying TCDD.

TABLE 4.7.1. CARBON TETRACHLORIDE TEST RESULTS

Parameter	Test 1	Test 2	Test 3
Chlorine Mass Loading (%)	35	40	35
Scrubber Effluent			
CCl ₄ (ppb)	1.27	5.47	3.26
mg/hr	2.29	9.85	5.87
Flare Exhaust			
CCl ₄ (ppb)	0.83	0.43	0.63
mg/hr	12.1	4.9	7.2
NO _x			
ppm(v/v)	106	92	81
lbs/hr	1.02	0.69	0.02
CO			
ppm(v/v)	48	57	81
lbs/hr	0.28	0.26	0.37
HCl			
mg/dscm *	(1)	137.7	247.7
kg/hr	(1)	0.25	0.44
Destruction Removal Efficiency	99.99998	99.99998	99.99998

(1) sample taken was invalidated due to plugging of sampling apparatus

*mg/dscm = milligrams per dry standard cubic meter.

TABLE 4.7.3. PCB TEST RESULTS

	Run 1	Run 2	Run 3
<u>Stack Gas Parameters</u>			
Total PCB, (1)	0.013	0.46	3.0
g/dscm* (2)	0.013	0.32	0.011
Total Dioxins, g/dscm	0.076 (3)	0.43	0.13
Total Furans, g/dscm	0.26	1.66	0.30
Total BaP, g/dscm	0.18	0.45	2.8
<u>Scrubber Effluent Parameters</u>			
Total PCB, ppb(1)	1.56	2.15	9.4
(2)	0.06	4.7	0.01
Total Dioxins, ppt	5.8	259	1.35
Total Furans, ppt	1.5	399	1.35
Total BaP, mg/L	0.04	0.92	2.0
<u>Destruction Removal Efficiency</u>			
PCB, Percent DRE			
(1)	>99.99999	99.99994	>99.9999
(2)	99.999999	99.99997	99.999999

(1) These values are based upon mono-decachlorobiphenyl.

(2) These values are based upon tri-decachlorobiphenol.

(3) No tetra or penta dioxins were detected at 0.05 ng on a GL column, except for run #1 where 0.06 ng tetra dioxin was reported.

*g/dscm = grams per dry standard cubic meter

Reference: Kolak, et al., 1986.

4.8 MOLTEN SALT DESTRUCTION

4.8.1 Process Description

The molten salt destruction process has been under development by Rockwell International since 1969 (Edwards, 1983). The original intent was to use the process to gasify coal. A variety of salts can be used, but the most recent studies have used sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3) in the 1,450°F to 2,200°F temperature range.

In addition to the Rockwell process, another molten salt process is under development. The State of New Jersey in late 1982 issued a contract to the Questex Corporation of New York to evaluate a mobile offsite earth decontaminator (MOSED), a waste treatment unit based on the molten salt destruction principle. A status report on the development of this device was presented at the 1985 Hazpro Conference (Leslie, 1985).

As shown in a schematic of the Rockwell process (Figure 4.8.1), the waste is fed to the bottom of a vessel containing the liquid salt along with air or oxygen-enriched air. The molten salt is maintained at an average temperature of 900°C (1,650°F). The high rate of heat transfer to the waste causes rapid destruction. Hydrocarbons are oxidized to carbon dioxide and water. Constituents of the feed such as phosphorous, sulfur, arsenic, and the halogens react with the salt (i.e., sodium carbonate) to form inorganic salts, which are retained in the melt. The operating temperatures are low enough to prevent NO_x emissions (Freeman, 1985; GCA, 1985; Edwards, 1983). Any gases that are formed are forced to pass through the salt melt before being emitted from the combustor. If particulates are present in the exhaust gases, a venturi scrubber or baghouse may be used (GCA, 1985; Edwards, 1983).

Eventually, the build-up of inorganic salts must be removed from the molten bed to maintain its ability to absorb acidic gases. Additionally, ash introduced by the waste must be removed to maintain the fluidity of the bed. Ash concentrations in the melt must be below 20 percent to preserve fluidity (Edwards, 1983).

Melt removal can be performed continuously or in a batch mode. Continuous removal is generally used if the waste feed rates are high. The melt can be quenched in water and the ash can be separated by filtration while

the salt remains in solution. The salt can then be recovered and recycled. Salt losses, necessary recycle rates, and recycling process design are strongly dependent on the waste feed characteristics (GCA, 1985; Freeman, 1985; Edwards, 1983).

Restrictive Waste Characteristics--

The ash content of the melt should be limited to 20 percent in order to maintain fluidity for a reasonable period of time. The process becomes inefficient and/or impractical for wastes of high ash content. Also, wastes with a low water content are destroyed more effectively.

Operating Parameters (Freeman, 1985; GCA, 1985)--

The following are typical parameters for the molten salt incinerator:

Waste Form	Solid or Liquid Wastes of Low ash and water contents
Operating Temperature	800 to 1000°C (1500° to 1850°F)
Average Residence Time	
Gas Phase	5 seconds
Solid (or Liquid Phase)	Hours
Energy Requirements	Fuel to burn waste (if not combustible) Electric power for blowers

4.8.2 Technology Performance Evaluation

Rockwell International has built two bench scale combustors (0.5 to 2 lb/hr), a pilot plant (55 to 220 lb/hr), and a portable unit (500 lb/hr) (Edwards, 1983). They have also built a 200 lb/hr coal gasifier based on the molten salt process.

Many wastes have been tested in the bench scale unit. Chemical warfare agents GB, Mustard HD, and VX have been destroyed at efficiencies ranging from 99.999988 to 99.9999995 percent. Other chemicals that have been destroyed using the molten salt combustion process include: chlordane, malathion, Sevin, DDT, 2,4-D herbicide, tar, chloroform, perchloroethylene distillation bottoms, trichloroethane, tributyl phosphate, and PCBs (GCA, 1985; Edwards, 1983).

TABLE 4.8.1. PCB COMBUSTION TESTS IN SODIUM-POTASSIUM-CHLORIDE-CARBONATE
MELTS [Edwards, 1983]

Temp (°F)	Stoichiometric air (%)	Concentration of KCl, NaCl in melt (wt %)	Extent of PCB destruction ^a (%)	Concentration of PCB in off-gas ^a (g/m ³)
1598	145	60	>99.99995	52
1526	115	74	>99.99995	65
1292	160	97	>99.99995	51
1643	180	100	>99.99993	59
1427	125	100	>99.99996	44
1427	90	100	>99.99996	66

^aPCBs were not detected in the off-gas, i.e., values shown are detection limits.

Reference: GCA, 1985; Edwards, 1983.

4.8.4 Process Status

Rockwell has constructed several molten salt units of varying sizes. The company has conducted extensive tests in two sizes of units; bench-scale combustors for feeds of up to 10 lb/hr wastes, and a pilot-scale unit for feeds of up to 250 lb/hr of wastes (Freeman, 1985).

Several developments will be needed if molten salt combustion is to be applied to dioxin-contaminated wastes. The 99.9999 percent DRE required by the current RCRA regulations must be demonstrated for dioxins, and additional testing with dioxin-contaminated wastes (both liquids and solids) needs to be performed on a larger scale. Research to develop more economical construction materials may also be required.

As indicated above, molten salt combustion is not currently practical for the treatment of dioxin-contaminated wastes. Additional research and development is required, but Rockwell has no plans for such further activity. The status of the New Jersey MOSED unit is not known.

4-81

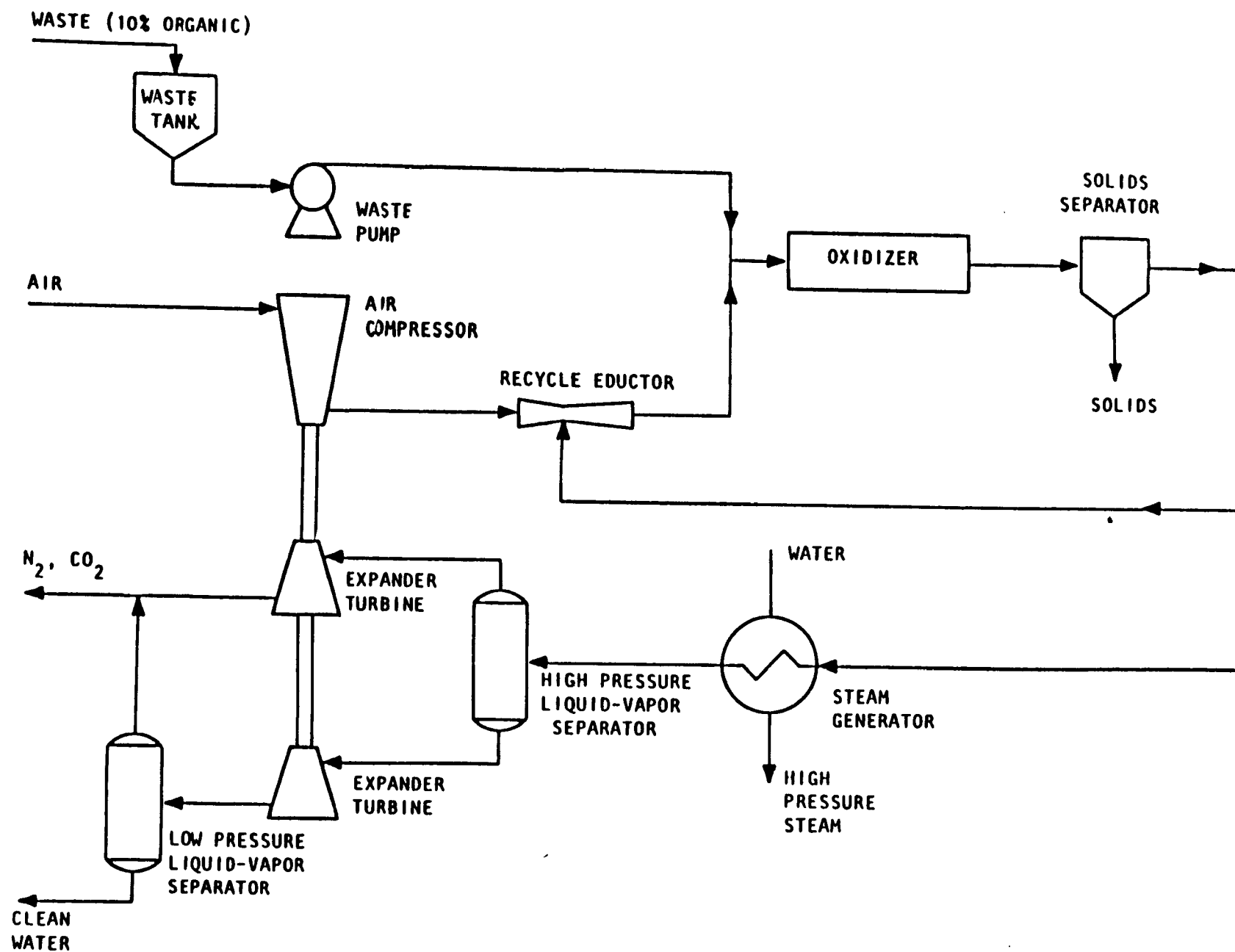


Figure 4.9.1. Process schematic for supercritical oxidation of an aqueous waste with a heating value of 1750 Btu/lb [Modell, et al., 1984].

4.9.2 Technology Performance Evaluation

Modar has built and tested bench scale supercritical water reactors for destruction of urea, chlorinated organics, and dioxin-containing wastes. Skid-mounted, transportable systems with a capacity of 50 gal/day have been designed as well as larger-scale stationary units.

A reactor, constructed of Inconel 628 and measuring 19.6 inches long with an inside diameter of 0.88 inches, was used to investigate urea destruction (GCA, 1985; GCA, 1984). Additional tests of the supercritical water oxidation process were conducted using a similarly constructed Hastelloy C-276 reactor with dimensions of 24 inches in length and 0.88 inch inside diameter (GCA, 1985; GCA, 1984). Tests on chlorinated organics were performed with this reactor. Table 4.9.1 summarizes the compositions of the various waste feeds used in the test runs. Liquid influents and effluents were analyzed for total organic carbon TOC by GC/MS (Modell, 1982). Gaseous effluents were analyzed by GC for low molecular weight hydrocarbons (Modell, 1982). The results of these analyses and the calculated destruction and removal efficiencies (DREs) are shown in Table 4.9.2. Chlorinated dibenzo-p-dioxins were searched for specifically, but none were found in the effluents.

A laboratory-scale trial burn was conducted using a feed consisting of synthesized dioxin added to trichlorobenzene (at 100 ppm concentrations) (Killiley, 1986). According to Modar, the process achieved greater than six nine's DRE based on the analytical detection limits for gas and liquid effluents (Killiley, 1986). Modar has performed studies on dioxin-contaminated soils for private clients, including a field demonstration using their pilot scale unit for the New York Environmental Conservation Department (Killiley, 1986). Although the results of these tests are not available for release at this time, the DREs for TCDD were reportedly greater than 6 nines (Killiley, 1986).

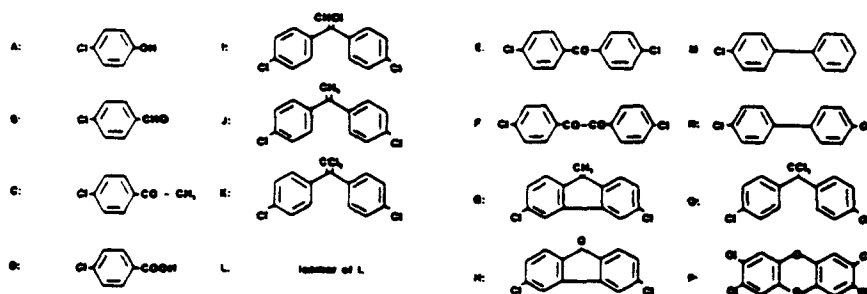
4.9.3 Costs of Treatment

The most significant operating cost factor is the cost of oxygen consumed (GCA, 1985). Although compressed air can be used as the source of oxygen, the cost of power as well as the high capital cost of appropriate compressors has

TABLE 4.9.2. SUMMARY OF RESULTS: OXIDATION OF ORGANIC CHLORIDES
[Modell, 1982]

Run No.	11	12	13	14	15
Residence time (min)	1.1	1.1	1.1	1.1	1.3
Carbon analysis					
Organic carbon in (ppm)	26,700.	25,700.	24,500.	38,500.	33,400.
Organic carbon out (ppm)	2.0	1.0	6.4	3.5	9.4
Destruction efficiency (%)	99.993	99.996	99.975	99.991	99.97
Combustion efficiency (%)	100.	100.	100.	100.	100.
Gas composition					
O ₂	25.58	32.84	37.10	10.55	19.00
CO ₂	59.02	51.03	46.86	70.89	70.20
CH ₄	--	--	--	--	--
H ₂	--	--	--	--	--
CO	--	--	--	--	--
Chloride analysis					
Organic chloride in (ppm)	876.	1266.	748.	775.	481.
Organic chloride out (ppm)	.023	.037	<.028	.032	.036
Organic chloride conversion (%)	99.997	99.997	99.996	99.996	99.993
GC/MS effluent analysis					
Compound B ^a (ppb Cl)	--	--	--	--	--
C	--	--	--	--	--
E	--	9	--	14	--
F	18	12	18	--	--
H	--	--	<4.	--	--
K	5	16	<5.	6	--
M	--	--	0.2	--	--
N	--	--	0.3	--	36
O	--	--	--	12	--

^aCompounds searched by GC/MS Analysis



These structures are included based on the chemical
of the starting material in the starting material
Compound F - No reported MS
Compound G - No MS available - literature

TABLE 4.9.3. MODAR TREATMENT COSTS FOR ORGANIC
CONTAMINATED AQUEOUS WASTES^a

Waste capacity		Processing cost	
gal/day	ton/day	\$/gal ^b	\$/ton ^b
5,000	20	\$0.75 - \$2.00	\$180 - \$480
10,000	40	\$0.50 - \$0.90	\$120 - \$216
20,000	80	\$0.36 - \$0.62	\$ 86 - \$149
30,000	120	\$0.32 - \$0.58	\$ 77 - \$139

^aBased upon an aqueous waste with 1800 Btu/lb heating value and inorganic solids of between 1% and 10%.

^bDoes not include energy recovery value of approximately \$0.05 per gallon.

Source: Sieber, 1986.

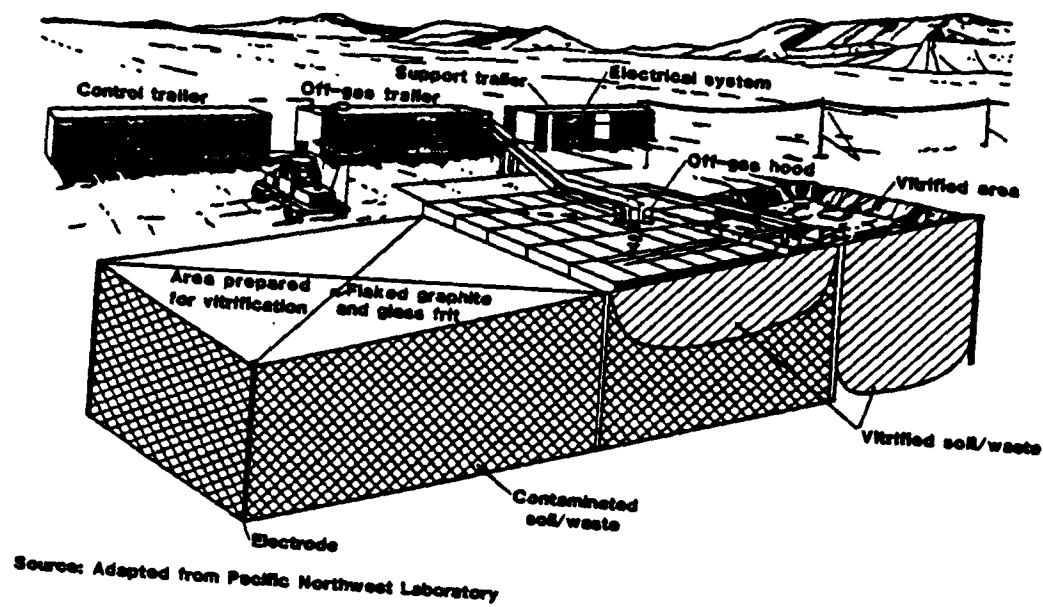


Figure 4.10.1. Schematic diagram of an in situ vitrification operation [Hazardous Waste Consultant, 1985].

costs such as labor and annual equipment charges (Oma, et al., 1983). Specifically, for variations in manpower levels, power source costs, and degree of heat loss it was determined that the costs for TRU waste vitrification ranges from 160 to 360 $\$/m^3$ to vitrify to a depth of 5 meters. These costs are a function of many variables but are most sensitive to variations in the amount of moisture in the soil and the cost of electrical power in the vicinity of the process. Figure 4.10.3, developed by PNL, illustrates the variation in total costs as a function of both electrical power costs and moisture content of TRU soil experimentally treated. The vertical line represents the value beyond which it is more cost effective to lease a portable generator.

Recently, PNL has assessed the cost implications for ISV treatment of three additional waste categories; i.e., industrial sludges and hazardous waste (PCB) contaminated soils at both high and low moisture contents (Buel, J., 1986). Representatives at PNL indicated that for industrial sludges with moisture contents of 55 to 75 percent (classified as a slurry), the total costs would range from 70 to 130 $\$/m^3$. Treatment of high (greater than 25 percent) moisture content hazardous waste-PCB contaminated soil would cost approximately 150 to 250 $\$/m^3$ versus costs of 128 to 230 $\$/m^3$ for low (approximately 5 percent) moisture content PCB contaminated soil.

As these recent data and past TRU waste cost data suggest, the moisture content of the contaminated material is particularly important in influencing treatment costs. High moisture content increases both the energy and length of time required to treat the contaminated material. Furthermore, PNL representatives suggest that treatment costs are also influenced by the degree of off-gas treatment required for a given contaminated material (i.e., ISV application to hazardous chemical wastes will likely not require as sophisticated an off-gas treatment system as would TRU waste treatment).

4.10.4 Process Status

As briefly indicated above in the "Cost" discussions, PNL has recently assessed the treatment and costs associated with hazardous waste contaminated soils (Buel, J., 1986). During the summer of 1985, tests were conducted for the Electric Power Research Institute (EPRI) on PCB contaminated soil. Note that while the draft report on these tests has been completed, it has not been published and/or made available to date. However, an EPRI project summary publication, dated March 1986, entitled "Proceedings: 1985 EPRI PCB Seminar" (EPRI CS/EA/EL 4480) has recently been made available to EPRI members. Preliminary results suggest that a destruction/removal efficiency (DRE) of six to nine nines was achieved from the off-gas treatment system overall, and that a vitrification depth of 2 feet was achieved. Additional information will soon be available to the public. PNL expects to continue with research in the area of hazardous waste soils.

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SECTION 5.0

NONTHERMAL TECHNOLOGIES FOR LISTED DIOXIN WASTES

This section reviews nonthermal technologies for treating dioxin wastes. Several of the technologies involve the addition of chemical reagents to degrade or destroy dioxin, e.g. chemical dechlorination, ruthenium tetroxide degradation, and degradation using chloriodides. Two technologies, ultraviolet (UV) photolysis and gamma ray radiolysis, involve the application of electromagnetic radiation to break down dioxin and other contaminants. There is also a subsection covering biodegradation. The remaining two treatment technologies discussed, solvent extraction and stabilization/fixation, are not destructive technologies, but rather represent pretreatment and temporary measures, respectively, for managing dioxin wastes.

The technologies that are included in this section are not evaluated in the same manner as the thermal technologies. Thermal technologies are primarily evaluated on the basis of six nines DRE, where DRE is a function of the concentration of a contaminant in the exhaust gas from the process. With nonthermal treatment there are generally no exhaust gases of significance. There are, however, other treatment effluents and residues which are major potential sources of dioxin emissions. Since EPA has proposed that these residues must contain less than 1 ppb of CDDs or CDFs in order to be land disposed, this will be the main criterion on which these technologies will be judged.

The use of the priority pollutant, naphthalene, proved to be a source of concern. Subsequent dechlorination processes were designed to utilize alternate reagents. For example, the Acurex Waste Technologies Corporation (now Acurex Corporation) developed a process (Dillon, 1982; desRosiers, 1983; Weitzman, 1986) which used a sodium-based reagent, prepared from proprietary but nonpriority pollutant constituents (Miille, 1981). The system operates by mixing filtered, PCB contaminated oil with the sodium-based reagent in processing tanks where the chemical reaction occurs. The two streams leaving the reactor are a treated oil containing no PCBs and a sodium hydroxide effluent. The entire PCB destruction process was designed to occur under an inert nitrogen atmosphere, however, Acurex found that this inert nitrogen blanket was not essential (Weitzman, 1986).

The SunOhio PCBX process, approved by USEPA in 1981, is a continuous, closed loop process utilizing a proprietary reagent to strip chlorine atoms from PCB molecules, converting the PCBs to metal chlorides and polyphenyl (polymer) compounds (Dillon, 1982; Jackson, 1981; SunOhio, 1985). PCB-contaminated mineral/bulk oils are first treated to remove moisture and gross contaminants. The PCB-contaminated oil is then mixed with the proprietary reagent and sent to the reactor where PCB destruction occurs. The mixture is then centrifuged, filtered, and vacuum-degassed. Effluent streams include treated oil, and polyphenyl/salt residues. The latter are solidified and then typically sent to a landfill. The entire system is mobile, as it is mounted on 40-foot tractor trailers. SunOhio commercially operates five mobile units.

Only limited information has been found relating to the PPM process; however, more is expected in the near future. From the available information, this mobile process destroys PCB contaminated oil through the aid of a proprietary sodium reagent (M. M. Dillon, 1982; des Rosiers, 1983). The reagent is added to the contaminated oil and left to react. The solid polymer formed by the reaction is filtered out of the oil. While this polymer is reportedly a regulated substance, it has been found to contain no PCBs and can readily be disposed of (M. M. Dillon, 1982). PPM currently has under development a dechlorination process designed to work on soils. However, no information is available on the process (personal conversation with L. Centofanti, PPM).

5.1.2 Technology Performance Evaluation

The Acurex process, while only applicable to contaminated PCB oils, has been extensively evaluated and is now commercially available via Chemical Waste Management (Weitzman, 1986). Tests by Acurex, during an EPA demonstration in the early 1980's, proved that this technology is effective in treating PCB-contaminated oils containing approximately 1,000 ppm to 10,000 ppm (1%)--reducing the PCB concentration to below detectable limits, about 1 ppm (Weitzman, 1982).

The SunOhio PCBX process has and will continue to be used only on liquid hydrocarbon streams (i.e., oil). The process cannot be used to treat contaminated soils. At present no tests have been performed on 2,3,7,8-TCDD, and it appears that this technology will continue to be used only on PCB contaminated oils or fluids (SunOhio, 1984). This process has reduced PCB contaminated transformer oil from 500 ppm to below detectable limits (1 ppm) in just one pass through the system (Weitzman, 1982). By passing a contaminated oil through the system three times, it is believed that the PCB concentration can be reduced from 3,000 ppm to below 2 ppm [Dillon, 1982; Jackson, 1981].

Performance data regarding the Goodyear process are limited. However, available information indicates that this process is capable of treating oils containing 300 to 500 ppm PCBs down to less than 10 ppm (Weitzman, 1982; Berry, 1981). The contaminated transformer or heat transfer oil is purified to this level within approximately 1 hour at ambient temperature. Like the Acurex/Chemical Waste Management and SunOhio dechlorination processes, the Goodyear process has only been demonstrated to be applicable to treatment of PCB-contaminated oils.

The "APEG-type" processes have been laboratory and, in select situations, field tested on PCBs and 2,3,7,8-TCDD-contaminated soil samples (Klee, A., et al., 1984; Peterson, R., et al., 1985 and 1986; Rogers, C. J., et al., 1985; Rogers, C. J., 1983). The APEG reagents used in these experiments have varied over the several recent years of research from the NaPEG-type, sodium-based reagents used in PCB destruction, to the KPEG-type, potassium-based reagents proven more efficient in 2,3,7,8-TCDD-type destruction.

TABLE 5.1.1. SUMMARY OF DATA SHOWING PERCENT REMOVAL OF TCDD FROM CONTAMINATED SOILS USING APEG DECHLORINATION PROCESS (Klee, A. et.al., 1984).

Days after application	Timberline ^a		Denny ^b	
	K-400	K-120	K-400	K-120
7 days	45%	46%	nm ^c	51%
28 days	35%	38%	12%	5%

^aInitial TCDD content equalled 277 28 ppb.

^bInitial TCDD content equalled 330 33 ppb.

^cnm = not measured

TABLE 5.1.2. SUMMARY OF DATA SHOWING PERCENT REMOVAL OF TCDD FROM CONTAMINATED SOIL AT DENNY FARM (Klee, A., et. al., 1984)

Days after application	Denny Farm Soil ^a	
	K-400 ^b	KM-350
1 day	8%	15%
7 days	19%	27%
14 days	16%	36%
21 days	25%	42%
28 days	22%	43%

^a The anomalies in the apparent decrease of the TCDD level of K-400 treated sample at day 14 was found not to be statistically significant.

^b K-400 reagent used in these experiments (vs. those shown in previous Table 5.1.1) was prepared from KOH pellets instead of a 66% aqueous KOH solution.

Additionally, it should be noted that during the summer of 1985, APEG-type reagents were tested by the U.S. EPA at the Shenandoah Stables dioxin-contaminated site to evaluate the dechlorination potential of these reagents on 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) under field conditions (Rogers, C. J., 1985). Results of these tests were not as promising as in the past using APEGs in the laboratory. Specifically, the APEG reagents were deactivated due to the fact that APEG is moisture sensitive. The soil moisture at Shenandoah was determined to be on the order of 18 to 21 percent by weight. These results, while not favorable, did point out that APEGs are extremely hygroscopic and that contact with moisture will eventually result in the deactivation of the APEG reagent.

Finally, results of the use of the Sea Marconi CDP-process are presented in Figure 5.1.1 and Table 5.1.5. Figure 5.1.1 shows that, at least in the beginning, the disappearance of 2,3,7,8-TCDD from the reaction mixture is linear with respect to time (Tundo, P., et al., 1985). The figure also indicates that mixtures containing higher weight PEGs promote a much more rapid decomposition of TCDD than mixtures containing lower weight PEGs. When a PEG with a molecular weight of 6,000 is used (square data points), greater than 99 percent decomposition of TCDD occurs in 30 minutes, while the use of a PEG with a molecular weight of 1,500 (circular data points) requires over two hours for an equivalent level of degradation. However, the reaction rate is also a function of temperature, and the reaction using PEG 6000 was carried out at 85°C versus 50°C for the PEG 1500 reaction. Therefore, based on the data presented in Figure 5.1.1, it is difficult to assess the full effects of higher molecular weight PEGs.

The data in Table 5.1.5 show the effect of temperature and different mixtures of reagents on the decomposition of TCDD. The first set of data represents the same conditions (PEG 6000 at 85°C) as those used to generate the square data points in Figure 5.1.1. As already mentioned, these conditions result in rapid decomposition of TCDD. The second set of data points was generated using a smaller quantity of PEG 6000 and adding a butyl ether compound to the reaction mixture. With this combination of reagents, greater than 99.9 percent decomposition of TCDD occurred in 30 minutes. For the third set of data, the reaction temperature was only 20°C, and the decomposition of TCDD was much slower than for all of the other uses. Only 50 percent decomposition occurred in 192 hours.

TABLE 5.1.5. DEGRADATION OF 2,3,7,8-TCDD UNDER DIFFERENT CONDITIONS
USING THE CDP-PROCESS (Tundo, P. et al, 1985)

REAGENTS (g)	TEMPERATURE (°C)	TIME (h)	DECOMPOSITION (%)
PEG 6000 (2.1)	85	0.5	99.4
K ₂ CO ₃ (0.5)		1.0	99.6
Na ₂ O ₂ (0.4)		1.5	99.75
		2.0	>99.9
PEG 6000 (1.3)	85	0.5	>99.9
K ₂ CO ₃ (0.5)			
Na ₂ O ₂ (0.2)			
BuO(CH ₂ CH ₂ O) ₂ H (0.2)			
PEG 6000 (1.8) ^a	20	72	30
K ₂ CO ₃ (0.4)		192	50
Na ₂ O ₂ (0.2)			

^a without n-decane: after homogenization at 80°C the reaction was solidified by cooling and kept at 20°C;

TABLE 5.1.6. PRELIMINARY ECONOMIC ANALYSIS OF
IN SITU AND SLURRY PROCESSES
(Peterson, R.L., et al., 1985)

Cost item	Cost, \$/ton soil	
	In situ	Slurry
Capital recovery	31	17
Setup and operation	65	54
Reagent	<u>200</u>	<u>20</u>
Total costs	296	91

corresponding to the absorption of a quantum (photon) of light is 95 kilo calories per gram-mole for UV light with a wave length of 3,900 angstroms and is 142 kilocalories per gram-mole for a wave length of 2,000 angstroms.

Table 5.2.1 lists the dissociation energies for many common chemical bonds, along with the wavelength corresponding to the energy at which UV photons will cause dissociation. As can be seen from the data in Table 5.2.1, bond dissociation energies range from a low of 47 kcal/gmole for the peroxide bond to a high of 226 kcal/gmole for the nitrogen triple bond. Of particular interest in the case of dioxins is the C-Cl bond, with a dissociation energy of 81 kcal/gmole, corresponding to an optimum UV wavelength of 353 nm. For reference purposes, this can be compared to the violet end of the visible spectrum with a wavelength of about 420 nm. Thus, the UV radiation of interest is in the electromagnetic spectrum close to visible light. This fact is important because it means that sunlight, which radiates strongly in the near visible wavelengths, might be a good source of UV photons which are capable of degrading many molecules.

It is not surprising then, that the use of sunlight to degrade certain toxic molecules has been noted by several researchers (des Rosiers, P.E., 1983; Zepp, R.G., 1977, Esposito, M.P., 1980; Crosby, D.G., 1971). In the case of 2,3,7,8-TCDD and other related compounds, the apparent mechanism is that a terminal C-Cl bond is broken by UV radiation, thus "dechlorinating the molecule" and converting it into less toxic compounds. (Note that this reaction mechanism is very similar to that of chemical dechlorination; i.e., a gradual and progressive substitution of the chlorine atoms.)

Efficient degradation appears to require the presence of a hydrogen donor, because while UV can cause the cleavage of the C-Cl bond, recombination can take place. However, if a hydrogen donor is present, it will also react and replace the chlorine on the molecule. For example, several researchers have noted that pure 2,3,7,8-TCDD and other chlorinated compounds degrade slowly or not at all when placed on inorganic substrates; but when suitable hydrogen donors are present, degradation in sunlight can be rapid (Crosby, 1978).

UV has been commercially used to kill micro-organisms such as bacteria, protozoa, viruses, molds, yeasts, fungi, and algae. Applications include process and drinking water disinfection and sterilization, pretreatment prior to reverse osmosis, and general algae and slime control.

Recently, UV photolysis has been viewed as a potential large-scale commercial mechanism to degrade toxic wastes. In attempting to obtain a simple, inexpensive, and effective soil detoxification method, the University of Rome evaluated the use of various cationic, anionic, and nonionic surfactants to solubilize 2,3,7,8-TCDD in an aqueous solution prior to photodegradation with sunlight or artificial UV light (Botre, C., 1978). Of the four surfactants, 1-hexadecylpyridium chloride or cetylpyridium chloride (CPC) was found to be the most effective solubilizing agent, as well as having the ability to enhance the subsequent photochemical degradation of 2,3,7,8-TCDD. Other solvents examined included sodium dodecyl sulfate (SDS), polyoxyethylene sorbitan monoleate (Teewn 80) and methanol.

In 1975, Velsicol Chemical Corporation (Chicago) experimented with removing 2,3,7,8-TCDD contamination from stockpiles of "Agent Orange", a defoliant used in Viet Nam (Crosby, D.G., 1978; des Rosiers, P.E., 1983). The 2,3,7,8-TCDD molecule was extracted by using n-heptane as a solvent, and exposing the solution to UV photolysis at 300-320 nm wavelength. The process resulted in a reduction from 1,900 ppb of 2,3,7,8-TCDD in the stockpiles to less than 50 ppb in end products (Zepp, R.G., 1977; Esposito, M.P., 1980). However, the process was not considered practical, and soon was discontinued.

Another UV degradation process that was developed in the early 1980s by the Atlantic Research Corporation was named Light Activated Reduction of Chemicals (LARC). This process involves bubbling hydrogen into an aqueous solution containing chlorinated hydrocarbons and then irradiating the solution with ultraviolet light to dechlorinate the contaminants. Work on this process was stopped several years ago for economic reasons (Kitchens, 1986).

More recently, three UV based processes have been described in the literature which may be viable for large-scale degradation of 2,3,7,8-TCDD, as well as other toxic chlorinated hydrocarbons. There are:

- the Syntex - IT Enviroscience process which involves UV photolysis preceded by solvent extraction,
- UV photolysis in combination with ozonation, and
- UV photolysis preceded by thermal desorption.

Section 5.2.2 contains a discussion of the performance of these three processes.

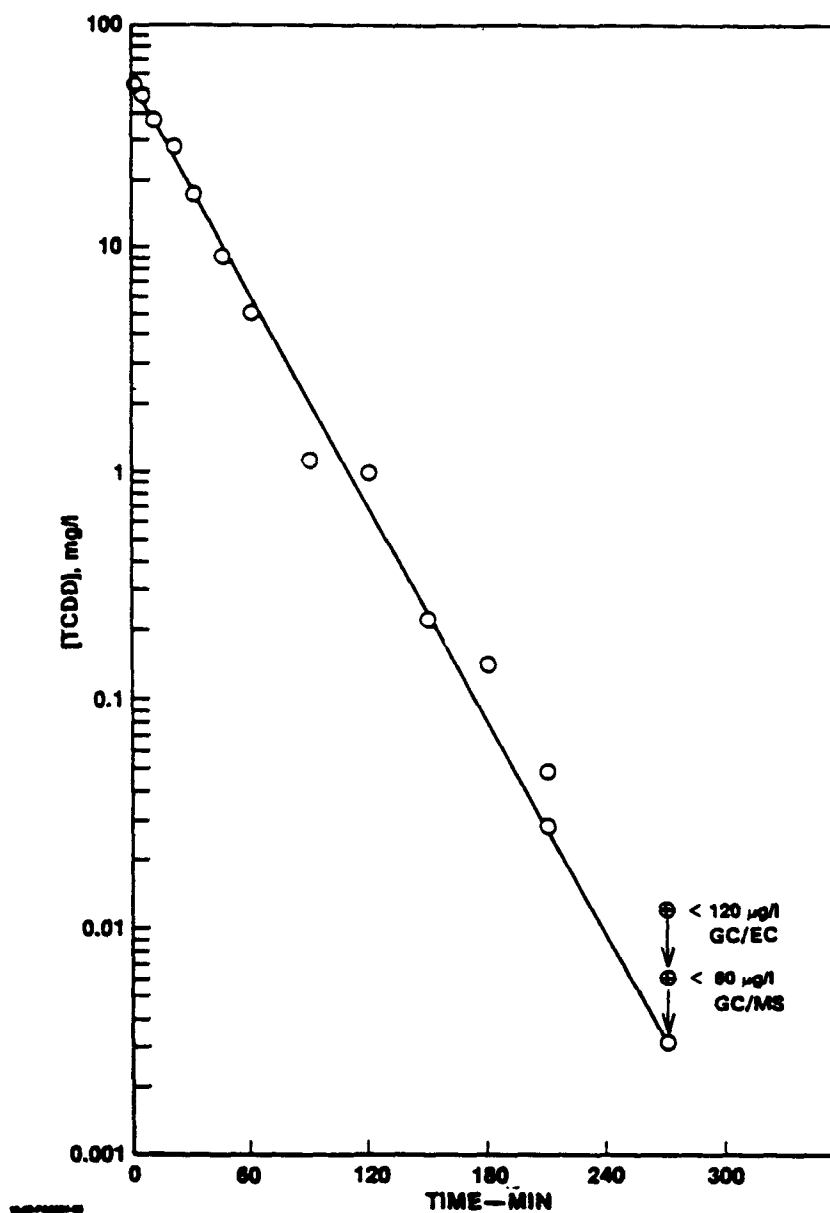


Figure 5.2.1. Rate of dioxin disappearance via UV irradiation of hexane extract of dioxin-contaminated still bottoms (Exner, J.H., 1982).

Ultraviolet (UV) Ozonolysis--

In 1979, it was shown (see Figure 5.2.2) by the California Analytical Laboratories and the Carborundum Company that ultraviolet activated ozone could successfully degrade 2,3,7,8-TCDD from the 1 ppb levels in solution to less than 0.4 ppb (Edwards, B.H., 1983). The procedure utilized to produce the results shown in Figure 5.2.2 consisted of bubbling ozone gas through the TCDD solution, which was then passed by UV lamps. The UV radiation lamps not only degraded the 2,3,7,8-TCDD directly, but integrated with ozone to enhance the oxidation of the 2,3,7,8-TCDD. No information was available regarding the waste products that were generated from this process.

UV ozonolysis has also been tested extensively in degrading PCBs down to levels of 1 ppb. An "ULTROX" pilot plant at a General Electric (GE) plant in Hudson Falls, New York, and another smaller installation at the Iowa Ammunition Plant, Burlington, Iowa, have proven the technical feasibility of this process on PCBs (Arisman, R.K., 1980; Edwards, B.H., 1983; Swarzn, E.M., 1982). Both of these plants mixed wastewater containing PCBs with ozone, then exposed the mixture to UV radiation in a mixing tank. Figure 5.2.3 shows a schematic of the pilot plant set up by GE to demonstrate the ULTROX UV/ozone system for PCBs.

Another UV ozonolysis process is called the "Oxyphoton" process. The process was reportedly capable of destroying a wide variety of toxic or organic compounds including PCBs, chlorinated dioxins, DDT, and many types of halogenated aliphatic and aromatic compounds (Worne, 1984). The process is carried out in stainless steel reactors and is capable of treating 60 to 1,800 gallons per hour of waste fluids. Liquid waste containing a proprietary catalyst is spray-atomized and premixed under pressure with oxygen containing 1 to 2 percent ozone prior to passage through the high intensity ultraviolet (UV) light.

One advantage to this vapor phase reaction process over the conventional liquid phase UV light processes is the rapid disintegration of the waste. Reaction rates are generally reported in the millisecond range. Presently, the oxyphoton process is on the "back burner", possibly because of unfavorable economics. No research efforts have directly involved 2,3,7,8-TCDD (Worne, 1984).

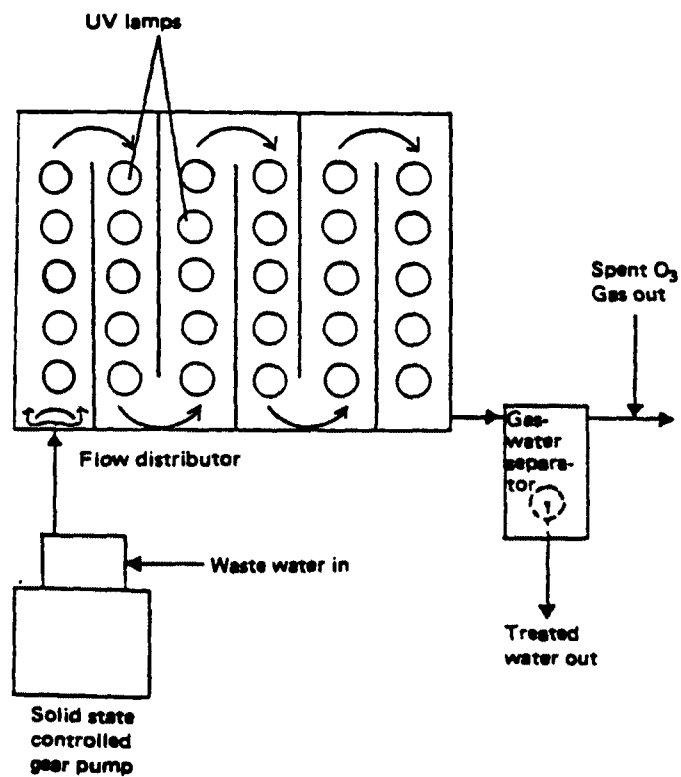


Figure 5.2.3. Schematic of top view of ULTROX pilot plant by General Electric (Ozone sparging system omitted) (Edwards, B. H., 1983).

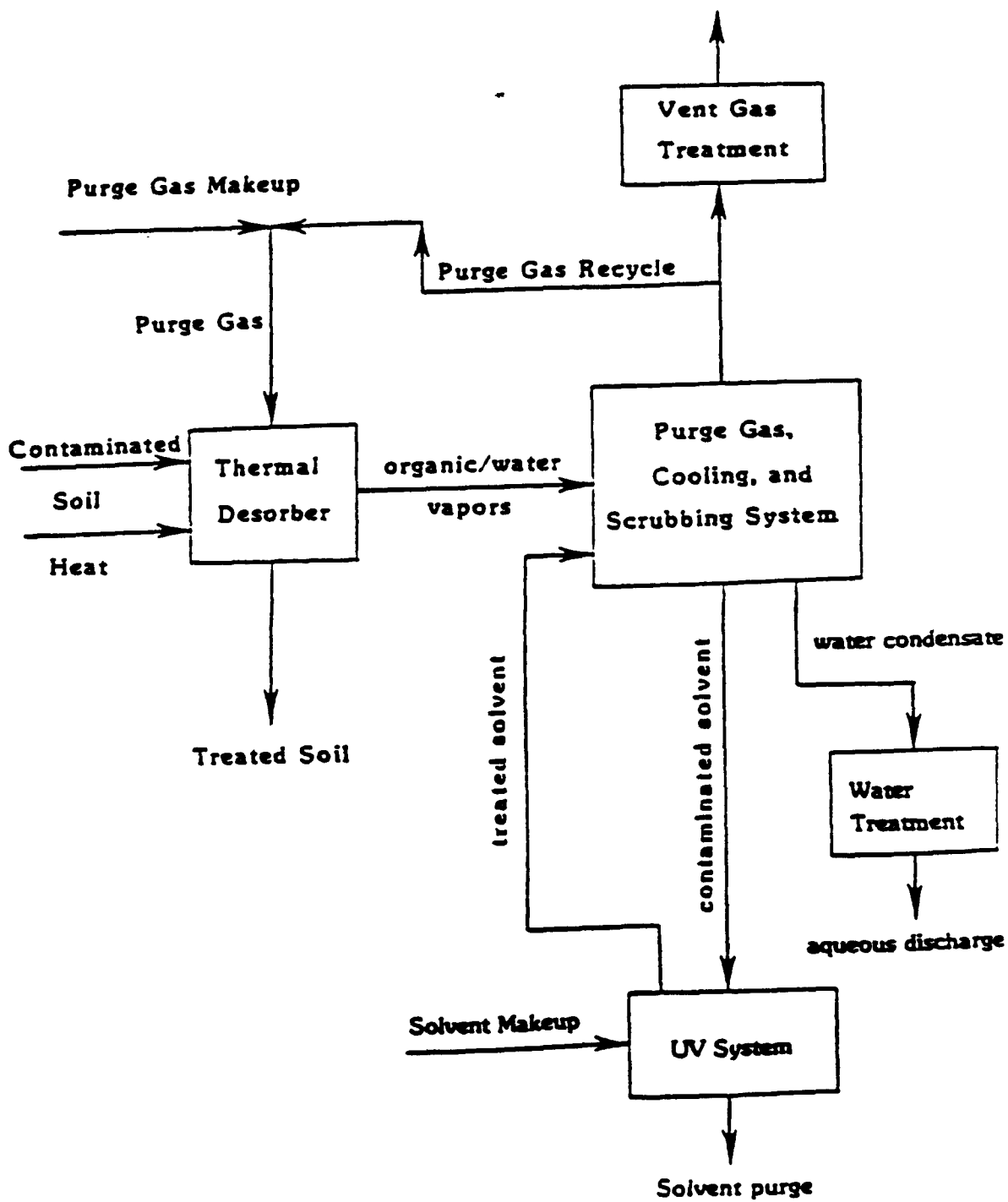


Figure 5.2.4. Thermal desorption, solvent absorption/scrubbing, UV photolysis process schematic (des Rosiers, P. E., 1985).

TABLE 5.2.3. DESIGN SPECIFICATIONS, CAPITAL, AND O&M COSTS FOR
40,000 AND 150,000 GPD ULTROX TREATMENT PLANTS
(50 ppm PCB feed-1 ppm PCB effluent)

<u>DESIGN SPECIFICATIONS</u>		
	40,000 GPD (151,400 LPD) <u>Automated System</u>	150,000 GPD (567,750 LPD) <u>Automated System</u>
<u>Reactor</u>		
Dimension, Meters (LxWxD)	2.5 x 4.9 x 1.5	4.3 x 8.6 x 1.5
Wet Volume, Liters	14,951	56,018
UV Lamps; Number 65 W	378	1179
Total Power, kw	25	80
<u>Ozone Generator</u>		
Dimensions, Meters (LxWxD)	1.7 x 1.8 x 1.2	2.5 x 1.8 x 3.1
kg Ozone/day	7.7	28.6
Total Energy required (kwh/day)	768	2544
<u>BUDGETARY EQUIPMENT PRICES</u>		
	40,000 GPD	150,000 GPD
Reactor	\$94,500	\$225,000
Generator	30,000	75,000
TOTAL	\$124,500	\$300,000
<u>O & M Costs/Day</u>		
Ozone Generator Power	\$4.25	\$15.60
UV Lamp Power	15.00	48.00
Maintenance (Lamp Replacement)	27.00	84.20
Equipment Amortization (10 Yrs @ 10%)	41.90	97.90
Monitoring Labor	85.71	85.71
TOTAL/DAY	\$173.86	\$331.41
Cost per 3785 Liters (with monitoring labor)	\$4.35	\$2.21
(without monitoring labor)	\$2.20	\$1.64

Source: Arisman, R.K. and Musick, R.C., 1980.

reduction of soils to enhance optimum solvent/soil contact. Solvent recycling allows reuse of expensive solvents and lowers concerns about disposal of contaminant-containing solvents. Distillation or vacuum stripping are the usual methods for cleaning solvents. In either case, the result is a concentrated volume of contaminant for eventual treatment or disposal (Weitzman, 1984; Firestone, 1984).

EPA has developed a mobile soils washing system (MSWS) process for extracting dioxin and other contaminants from soil. The EPA-developed MSWS contains two basic components, as summarized below from IT Corporation, 1985 and as shown in Figure 5.3.1. These components are a Drum Screen Scrubber and a Counter-Current Chemical Extractor. The Drum Screen unit automatically loads previously excavated soil (particle sizes less than 1 inch) into the system where it passes through high pressure streams of extractant solution and a "soaking zone". The high pressure streams are designed to wash sands and stones and to separate fines for further, high energy extraction. Sands and stones are discharged from the Drum Screen and the fines are pumped continuously into the Counter-Current Extractor, which consists of four high-shear mixing chambers. As the fine soil (less than 2 mm) leaves each chamber, it is separated from its solvent carrier before it enters the next chamber. The design capacity of the MSWS is 18 cubic yards of soil per hour.

5.3.2 Technology Performance Evaluation

Solvent extraction of chemical substances from soil has been commonly used in the mining industry and has been demonstrated for extraction of bitumen from tar sands (Cotter, 1981). Currently, the only full-scale process that has attempted to use solvent extraction for dioxin molecules dealt with a contaminated slurry. In this instance, the dioxin molecule (2,3,7,8-TCDD) was extracted from distillation still bottoms at the Syntex Agribusiness facility in Verona, Missouri. IT Enviroscience was contracted by Syntex to develop a safe and effective method for removing approximately 7 kg of dioxin from about 4600 gal of waste (Exner, J.H., et al 1982). The treatment process designed by IT involved the separation (extraction) of dioxin using a solvent, followed by the photolytic dissociation of the carbon-halogen bond (see Section 5.2). The solvent extraction phase of this project, as briefly described below, involved several laboratory, miniplant, and scale-up operations.

Specifically, IT Enviroscience performed tests on hexane, tetrachloroethylene and o-xylene to determine which solvent would best remove the dioxin molecule and, once removed, would allow the dioxin molecule to be effectively degraded via the photolytic step. Their results showed that hexane extraction of the subject wastes performed better overall than the other two solvents. Based upon these results, a large-scale reactor vessel was designed and constructed. In 1980, this reaction vessel processed several 160-gal batches of the dioxin-containing waste resulting in a reduction of 2,3,7,8-TCDD-concentrations of from 340 to 0.2 ppm via six hexane extractions.

IT Corporation, under the auspices of EPA, has also prepared additional laboratory experiments to assess the suitability of the EPA Mobile Soils Washing System (MSWS) for use in extracting dioxin from contaminated soils (IT Corporation, 1985). The MSWS was designed to use water, or water with non-toxic and/or biodegradable additives, as an extractant solution. Non-hazardous additives are required because some residual solution will always remain with the discharged soil. Because of this requirement, various additives, such as surfactants and fuel oil, were evaluated in the laboratory for the removal of dioxin from soil. Although laboratory results indicated that 60% to over 90% of the 2,3,7,8-TCDD could be removed by the Soils Washing System, in most cases (soils initially containing over 100 ppb of dioxin) the washed soil would still contain residual dioxin in excess of the 1 ppb guideline for decontamination. Similarly, while other experiments using Freon and Freon-methanol combinations proved promising, the target residual dioxin levels could not be achieved under the test conditions. It was concluded that the major obstacle to removing dioxin from the soils was that dioxin binds strongly to small soil particles. The soils on which the MSWS was tested were from the Denney Farm in Missouri. These soils contained a high percentage of extremely fine materials (33% less than 5 microns, 26% less than 1 micron). For materials with larger grain size, such as sands and gravels, the process may be viable (IT Corporation, 1985).

In other laboratory experiments, both aqueous and organic solvents have been tested on 2,3,7,8-TCDD-contaminated soil. In 1972, Kearney used a 1:1 hexane: acetone solvent solution on 2,3,7,8-TCDD (labeled with carbon isotopes) in loamy sand and silty clay-loam soils. Electron-capture gas

TABLE 5.3.1. SOLUBILIZATION OF TCDD (Botre, C., et al. 1978)

Solubilizer	Experiments on soil ^a		Experiments on pure TCDD ^b			
	Surfactant concn	Solubilized TCDD (%)	Surfactant conc	Solubilized TCDD (%)	Surfactant conc	Solubilized TCDD (%)
MeOH	-	97.5	-	100	-	100
CPC	0.05M	75.0	0.02M	75	0.05M	78
SDS	0.05M	60.0	0.02M	71	0.05M	75
Tween 80	2% w/v ^c	45.0	1% w/v ^c	72	2% w/v ^c	73

^aEach 90-g sample contained initially 6.3 µg of TCDD.

^bInitial amount of TCDD: 40.90 µg.

^cPercent weight to volume

found in a soil matrix, in situ degradation is a more practical alternative. In addition to the various modes of treatment, biodegradation can be effected by a number of different types of micro-organisms. These include:

- aerobic bacteria;
- anaerobic bacteria;
- yeast; and
- fungi.

Following a discussion of the environmental degradation of TCDD, examples of research on the application of several of these modes of treatment and types of micro-organisms will be presented.

Degradation of 2,3,7,8-TCDD is a slow process, overall, in the natural environment. Natural degradation is primarily due to biodegradation and photochemical (UV) breakdown. A wide variety of half-lives have been reported. The observed half-life for uncontrolled biodegradation of 2,3,7,8-TCDD has been reported as 225 and 275 days by the U.S. Air Force (Young, 1976), although a separate analysis of the same data yielded half-lives ranging from 190 to 330 days (Commoner, 1976). Another study reported that half-life is affected by concentration, being greatly reduced at high concentrations (Bolton, 1978). In fact, half-lives are probably significantly greater than those reported, as most early research did not account for the strong tendency for 2,3,7,8-TCDD to bind to soil particles. Strongly bound 2,3,7,8-TCDD would not have been detected analytically and biodegradation assumed incorrectly to be the cause of its absence.

Studies at Seveso, Italy indicate that the half-life of 2,3,7,8-TCDD increases with its time in the soil, because of its tendency to become more tightly bound to soil and organic matter (DiDominico, 1980). DiDominico found that half-life calculations made 1-month after the Seveso accident predicted a 10 to 14-month half-life, but 17 months after the accident, the half-life of 2,3,7,8-TCDD in the soil had increased to more than 10 years.

In a study performed for the Air Force, 99 percent of the 2,3,7,8-TCDD sprayed as a constituent of defoliants was still present 12 to 14 years after application (Young, 1983). Although natural degradation seems to proceed

TABLE 5.4.1. MICRO-ORGANISMS WITH KNOWN CAPABILITY FOR
DEGRADING 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN

	Researcher
<i>Nocardioopsis</i> sp.	Matsumura, 1983.
<i>Bacillus megaterium</i>	Matsumura, 1983.
<i>Beijerinckia</i> B8/36 ^a	Klecka, 1980.
<i>Pseudomonas</i> , sp. ^b	Klecka, 1979.
<i>Biejerinckia</i> , sp. ^a	Klecka, 1980.
<i>Phanerochaete chrysosporium</i> ^c	Bumpus, et al., 1985.

^aOxidation of dibenzo-p-dioxin and several mono-, di-, and trichlorinated dibenzo-p-dioxins was reported.

^bMetabolism of dibenzo-p-dioxin was observed.

^cWhite rot fungus.

Ongoing Research--

There have been several more recent research projects concerning the biodegradation of 2,3,7,8-TCDD and related compounds. Some of the more significant ones are discussed below.

White Rot Fungus (Bumpus et al., 1985)--

One method that has received a large amount of attention has involved the study of the ability of the fungus, P. chrysosporium, to degrade recalcitrant organopollutants, one of these being 2,3,7,8-TCDD. P. chrysosporium is a lignin-degrading white rot fungus. This organism secretes a unique hydrogen peroxide-dependent oxidase capable of degrading lignin, a highly complex, chemically resistant, nonrepeating heteropolymer. The enzyme catalyzes the formation of carbon-centered radicals which react with oxygen to initiate oxidation. The low molecular weight aromatic compounds formed may then undergo further modification or ring cleavage and eventually be metabolized to carbon dioxide.

Several properties of P. chrysosporium make it a candidate for the degradation of the more recalcitrant organopollutants such as 2,3,7,8-TCDD, DDT, lindane and PCBs. First of all, the organism is able to degrade lignin, chlorinated lignin and chlorinated lignin-derived by-products of the Kraft pulping process. Secondly, low levels of pollutant (such as may exist in contaminated soil) do not repress the production of enzymes required for degradation. Thirdly, the organism is not substrate-specific and therefore can attack and degrade a wide variety of structurally diverse, recalcitrant compounds. Finally, P. chrysosporium is a highly successful competitor in nature, especially when the carbon source is lignin. Consequently, competition by other organisms will be minimal if wood chips or sawdust are added as a supplement to the waste material.

Results of laboratory tests using P. chrysosporium to degrade several different compounds are shown in Table 5.4.2. In 10 ml cultures containing 1.25 nmoles of the ^{14}C -labeled 2,3,7,8-TCDD substrate, 27.9 pmoles were converted to $^{14}\text{CO}_2$ within 30 days and 49.5 pmoles within 60 days, representing 4.96 percent metabolism. The remaining carbon atoms should have either been incorporated into the organism or been present as intermediates in the pathway between 2,3,7,8-TCDD and CO_2 . This conclusion is based on more

detailed studies of the degradation of DDT which indicated that after 30 days 4 percent of the original DDT was evolved as CO₂, when approximately 50 percent of the DDT had been degraded. In the case of DDT, greater than 99 percent degradation had occurred after 75 days.

Matsumura and Quensen (Quensen and Matsumura; 1983, Quensen, 1986)--

Research has been conducted at the Pesticide Research Center of Michigan State University in which low concentrations of 2,3,7,8-TCDD were metabolized by pure cultures of *Nocardiosis* spp. and *Bacillus megaterium*. In these experiments TCDD in solvent was added to flasks containing the pure cultures, and after a period of 1 week, the contents were extracted and analyzed for TCDD and metabolites.

Several conclusions were drawn from the study. One of these, as substantiated by detail in Table 5.4.3, is that the choice of solvent used to dissolve TCDD and add it to the culture medium has a significant effect on the degradation of TCDD. The use of ethyl acetate or dimethyl sulfoxide (DMSO) resulted in significantly higher degradation than when corn oil or ethanol were used. Another conclusion that was drawn is that lowering of alternative carbon sources increases the degradation of TCDD. The proportion of TCDD metabolized by *B. Megaterium* increased dramatically when the amount of soybean extract in the medium was reduced from 1.6 to 0.4 percent and ethyl acetate was used as the solvent. Finally, analog-induced metabolism of TCDD by including naphthalene or dibenzofuran in the culture medium proved to be ineffective.

In addition to the pure culture experiments, TCDD degradation in soil by naturally occurring micro-organisms was also studied. TCDD was added to three different types of soil and after 0, 2, 4, and 8 months of incubation, soil samples were extracted and the levels of TCDD and metabolites were determined. Very little metabolism of TCDD occurred in any of the soils over the 8 month period. This was true regardless of which solvent was used to add TCDD to the soil system. Dimethyl sulfoxide, ethyl acetate and 10 percent ethanol were used. They surmised that the resistance to degradation was due to the fact that TCDD binds tightly to soil thereby limiting the rate of cellular uptake.

Kearney and Plimmer (Kearney, 1984)--

A biological process to detoxify 2,3,7,8-TCDD-contaminated soils is being evaluated at the Agricultural Research Center in Beltsville, Maryland. Work is based on the observation that soil micro-organisms have the ability to degrade highly chlorinated organics that have been pretreated with ultra-violet (UV) radiation. Pretreatment with UV radiation removes chlorine from the 2,3,7,8-TCDD molecule in the presence of a proton donor, and the resulting dibenzo-p-dioxin molecule can then be biodegraded.

Laboratory studies have involved subjecting solutions of chlorinated organics to UV radiation before adding them to the soil where biodegradation could take place. Kearney and his colleagues have since experimented with a prototype system that includes a 55-gallon stainless steel drum as a holding tank and a commercial water purifying unit as the UV source. Kearney's process focuses on cleaving the chlorine-carbon bonds in the chlorinated organic compounds by the following procedures:

1. Expose a dilute aqueous solution (i. e., 1 ppm 2,3,7,8-TCDD) to ultra-violet light (UV) for at least 1 hour (Photo-Chemical Reaction).
2. While irradiating, bubble oxygen through the solution to speed up the chlorine-carbon bond break up (Ozone Reaction).
3. Pour or spray irradiated solution over soil containing the test micro-organisms (Biodegradation).
4. Determine the percent degradation by monitoring the amount of carbon dioxide generated.

Recent studies (1981) have yielded the following results:

- 80 percent degradation of 2,4,5-T over 1 month;
- 80 percent degradation of PCB over 1 month;

TABLE 5.4.4. SUMMARY OF RESEARCH PROJECTS ON BIODEGRADATION OF TCDD SURROGATES

Researcher	Compounds tested	Type/Name of micro-organism	Type of process	Performance	Reference
University of Illinois Medical Center	2,4,5-T; 2,4-D, Chlorophenols; research has been funded for TCDD	<u>Pseudomonas Cepacia</u> , AC1100	micro-organisms developed by acclimation to 2,4,5-T in a chemostat; bacteria also can be applied to soil	up to 98% degradation of 2,4,5-T; reduction of 2,4,5-T in soil from 1000 ppm to 30 ppm in one week	Chosai, et al., 1985; Kilbane et al., 1983; Tomasek and Chakrabarty, 1985
Michigan State University	2,4,5-T, chlorinated phenols	unidentified anaerobic bacteria	would probably involve the use of an anaerobic digester	capable of removing chlorine atoms from the chlorobenzoate molecule	Tiedje, 1984
Sybron Corporation, Salem, Virginia	3,4-Dichlorophenol	<u>Pseudomonas Stutzeri</u>	addition of microbes in powdered form to contaminated site	lab testing has shown degradation at 3,4-DCP concentrations of 50-100 ppm	Davis, 1984; Goldsmith, 1986
Groundwater Decontamination Systems, Inc., Waldwick, N.J.	acetone; methylene chloride; n-butyl alcohol; 1,4-dichloro-dibenzo-p-dioxin (1,4-DCDD)	unknown	activated sludge system from which micro-organisms are injected into groundwater	600-700 ppm of contaminant reduced to less than 6 ppb for industrial organics	Macassa, 1983
Louisiana State University, Hazardous Waste Research Center	2,4-D and 2,4,5-T	<u>Pseudomonas</u> (only identifiable at the genus level), <u>Alcaligenes eutrophus</u>	laboratory scale batch reactors	demonstrated growth of micro-organisms using 2,4-D as sole carbon source	Roy and Mitra, 1986
University of Minnesota	2,4-D; 3,5-dichlorobenzene (3,5-DCB)	sewage treatment plant sludge was the source of innoculating after acclimation, the <u>Pseudomonas</u> species was predominant	laboratory batch reactors and chemostats	micro-organisms were capable of utilizing 2,4-D and 3,5-DCB as the sole substrate at concentrations between 10ug/l and 100mg/l	Kim and Maier, 1986

temperature, pH, and wood chip type and size (the substrate on which the micro-organism is grown) will be varied to determine optimum growth conditions (Sferra, 1986). After this, the white rot fungus will be tested in soil plots containing TCDD. This means that the application of even a promising micro-organism such as *P. Chrysosporium* to actual waste will not occur for several years, and only then if it proves to be successful in lab-scale testing.

Several treatment methods described above have been demonstrated to be applicable to the treatment of compounds that are similar to 2,3,7,8-TCDD, such as chlorophenols and 2,4,5-T. They have not, however, been tested either in the lab or the field on waste containing TCDD. In the case of the Sybron Corporation work, it has been difficult to obtain samples of waste with which to test their process in the lab, and it has also been difficult to test their process at actual sites of TCDD contamination (Goldsmith, 1986). One of the reasons for the difficulty in testing microbial processes on actual waste sites is the issue of releasing genetically altered micro-organisms to the environment.

In summary, the feasibility of biodegradation of 2,3,7,8-TCDD as a treatment technology is still in question. Most investigations have been performed in the laboratory, and the efficiency of a large scale treatment process is unknown. There are many advantages associated with biotreatment which make continued investigation advisable:

- The end products of complete biodegradation are nontoxic.
- Some processes may be accomplished onsite without soil excavation. However, use of solvents which could potentially cause uncontrolled mobilization of 2,3,7,8-TCDD must be avoided.
- Biological treatment appears to be effective at low 2,3,7,8-TCDD concentrations.

In addition, biotreatment could be coupled with other treatment processes to make them both more efficient. For instance, the sodium polyethylene glycol (NaPEG) process might be modified to in-situ treatment with the use of micro-organisms to degrade the dechlorinating solvent and the residual nonchlorinated and less chlorinated dibenzo-p-dioxins.

TABLE 5.5.1 SUMMARY OF STABILIZATION PROCESSES FOR TREATING
HAZARDOUS WASTES (M. E. Tittlebaum, et al., 1985)

Classification	Process sponsor (process name)	Stabilization agents	Wastes treated
Cement-based	Chemfix	Cement, soluble silicates	Inorganics
	Stablex (Sealosafe)	Cement, flyash	Inorganics
	Stabatrol (Terra-Tite)	Cement, additives	Inorganics
Lime-based or pozzolanic	Dravo Lime (Calcilox)	Lime, additives	FGD sludges
	International Mill Service	Lime	Metal slags
	IU Conversion Systems	Lime	FGD sludges
	Soil Recovery Systems	Lime	Misc.
	Sludgemaster	Lime, additives	Misc.
Thermoplastic	Werner and Pfleiderer	Asphalt	Misc.
	Southwest Research Inst. (Sulfex)	Sulfur, modifiers	Misc.
Thermosetting polymer	Dow Chemical	Polyesters, polyvinyls	Radioactive
	Newport News Industrial	Polyesters	Radioactive
Macro- encapsulation	Environmental Protection Polymers	Polyolefins	Soluble toxics
	TRW Systems	High-density polyethylene	Misc.
Self-cementing	Sludge Fixation Technology (Terra-Crete)	Calcium sulfite or sulfate	FGD sludges
Classification	None specified	Glass or ceramics	Radioactive
Other	ARDECCA	Proprietary	Oil field wastes
	Anschutz Corp. (Ansoorb)	Clay-like material	Misc.

Inorganic Stabilizers--

Lopat Enterprises, Inc., of Asbury Park, New Jersey has developed a product called "K-20" (McDaniel, 1983). K-20 is an inorganic mixture of at least eight chemicals (McDaniel, 1983). No further information on its content is available at this time. Lopat, Inc., has a patent pending for K-20, which was originally developed as a sealant for leaky basements (Goldensohn, 1983). Recent investigations have shown evidence that dechlorination of chlorocarbon contaminants may occur when K-20 is used as an encapsulant (Jiranders, 1984).

Pretreatment Requirements/Restrictive Waste Characteristics--

Stabilization is more frequently used for inorganics because organics tend to interfere with the physical and chemical processes which are necessary to bind the materials together (Spooner, 1985; Hazardous Waste Consultant, 1985; GCA, 1985). Wastes with greater than 10 to 20 percent organic content are generally not recommended for treatment by stabilization.

5.5.2 Treatment Performance Evaluation

In 1985, the Solid Waste Research Division of the Disposal Branch of the U.S. EPA sponsored a study to find the optimum mixture of asphalt and soil cement that will stabilize 2,3,7,8-TCDD-contaminated soil (Vick, 1985). The Portland Cement Institute and the Asphalt Institute will be reviewing the work. In the laboratory, stabilized soil underwent a leach test designed by Battelle- Columbus Laboratory. A structural integrity test was suggested, but not undertaken, because the soils are not expected to be subject to large loads (even though strength tests are often an indication of durability).

JRB Associates, under the sponsorship of the U.S. EPA, conducted a field test of cementitious and asphaltic stabilization techniques in the State of Missouri during 1985 (Vick, 1985; Ellis, 1986). The objectives of this testing program included:

- evaluating the cost-effectiveness of the processes;
- developing optimum soil/stabilizer ratios and mixing conditions; and
- assessing the viability of successful field implementation.

TABLE 5.5.2. SOIL TYPES USED TO TEST PORTLAND CEMENT
AND EMULSIFIED ASPHALT/LIME STABILIZATION
TECHNIQUES

Site	Description	Soil type	TCDD concentration
Minker	Residential area with steep, sloping banks that drain into a nearby creek	Sandy loam	700 ppb
Piazza Road	Roadside material	Sandy loam	640 ppb
Sontag Road	Roadside material, with considerably greater percentage of fine particles (silt and clay) than Piazza Road sample	Sandy silty loam	32 ppb

(Technical Resources, Inc., 1985).

The University of Maryland is currently performing controlled tests on the ability of K-20 to decontaminate soils by encapsulation and/or dechlorination using several chlorinated hydrocarbons including 2,3,7,8-TCDD. The U.S. EPA in Cincinnati, Ohio is also running some tests on the ability of K-20 to degrade 2,3,7,8-TCDD in soil. The results of the last two sets of tests may help to evaluate the effectiveness of this encapsulation agent.

5.5.3 Costs of Treatment

To date, stabilization/fixation processes have not been fully tested and cost effectiveness has not been documented. Organic wastes are generally more practically disposed of via other technologies such as incineration. Fixation becomes more cost-effective when the organic content of the waste is small, thereby making incineration less feasible (e.g., 2,3,7,8-TCDD-contaminated soils).

5.5.4 Process Status

Application of stabilization/fixation processes to organic wastes is a relatively recent development, because organic wastes generally lend themselves better to other treatment processes such as incineration or biodegradation. Preliminary studies of contaminated soil suggest that an emulsified asphalt-lime combination may be an effective interim remedial measure for stabilization of dioxin-contaminated soils (Vick, 1985; Ellis, 1986).

Further studies plan to investigate the leaching potential and performance of formulations using uncompacted soils (Vick, 1985). Future goals are to develop a procedure whereby temporary in-situ stabilization could be followed by soil/stabilizer removal and complete stabilization or fixation at an offsite facility.

Tests have also been done on synthetic wastes containing PCDDs. In one of these experiments, 2,7-DCDD, when mixed with RuO_4 in a carbon tetrachloride solution was determined to have a half-life of 215 minutes at 30°C; the half-life decreased to 38 minutes at 50°C. The oxidation of 2,3,7,8-TCDD proved to be a slower reaction; at 20°C it had a half-life of 560 minutes, while at 70°C the half-life decreased to slightly less than 15 minutes.

5.6.3 Costs of Treatment

Due to the current level of development of this technology, no cost data are available. Major costs would be for energy to heat up the material to be treated, and the cost of the chemical reagents. Pretreatment, extraction and post-treatment costs are unknown.

5.6.4 Process Status

To date, this method of degrading TCDD has only been performed on a laboratory scale. While these studies have shown that RuO_4 has the ability to degrade 2,3,7,8-TCDD, the reaction end products have not been identified. In addition, the only work reported has involved either the use of water or CCl_4 as the solvent. Water is not very effective, and the application of carbon tetrachloride to soil would not be environmentally acceptable. Thus, the use of other solvents should be investigated.

This technology will require considerable work before it can be applied in the field. The high cost of ruthenium tetroxide and the toxicity of process residuals may limit application of this technology. Its potential (if any) probably lies in the area of detoxification of glassware or purging of industrial reactors (des Rosiers, 1986).

5.7 CHEMICAL DEGRADATION USING CHLOROIODIDES

5.7.1 Process Description

A method for the degradation of substances containing both aromatic rings and ether bonds was reported in 1979 (Botre, 1979; des Rosiers, 1983; Esposito, 1980). This is of current interest because 2,3,7,8-TCDD contains

decomposition of 2,3,7,8-TCDD without irradiation. This latter method utilizing chloriodides is therefore more suitable for degrading bulk solutions.

5.7.2 Technology Performance Evaluation

No commercial processes utilizing chloriodides for decomposition of 2,3,7,8-TCDD are known to exist. However, experiments illustrating the use of surfactants containing chloriodides for the cleavage of ethers have been accomplished. These experiments have been performed on substances such as xanthene, benzofuran, and 2,3,7,8-TCDD (Botre, 1979). All substances tested confirmed that chloriodides aided in the decomposition. This discussion will be limited to the results from experiments on 2,3,7,8-TCDD.

In one study, solutions containing 2,3,7,8-TCDD in benzene were vacuum evaporated and the residues were treated with aqueous surfactant solutions (Botre, 1979). Two chloriodide derivatives were used in the surfactant solutions: benzalkonium chloriodide, and cetylpyridinium chloriodide. When benzalkonium was used, a 71 percent decomposition of 2,3,7,8-TCDD was observed. When cetylpyridinium chloriodide was used, a 92 percent decomposition of 2,3,7,8-TCDD was achieved. Reaction products included chlorophenols, phenols, and 2-phenoxychloro-phenols. Quantitative information was not available for these substances. The results were obtained under ideal conditions, so extrapolations to actual decontamination should be made with great care.

Contaminated soil samples from Seveso, Italy were also treated (Botre, 1979; des Rosiers, 1983; Esposito, 1980). Samples were prepared by treating the soil with solutions containing surfactant micelles with chloriodides and micelles without chloriodides. A benzalkonium chloride micellar solution showed approximately a 14 percent decomposition of 2,3,7,8-TCDD. A solution containing benzalkonium chloriodide in a micellar solution showed a decomposition of 52 percent of 2,3,7,8-TCDD. Thus, the addition of chloriodides to micellar surfactant solutions greatly enhances the decomposition of 2,3,7,8-TCDD. This study did not specify whether or not exposure to UV radiation occurred. UV radiation may or may not enhance decomposition significantly, depending on the experimental configuration.

5.8 GAMMA RAY RADIOLYSIS

5.8.1 Process Description

Gamma rays are electromagnetic waves of energy (photons) similar to x-rays, except that they are commonly generated in different ways and are of much higher energy. In fact, gamma rays possess the highest energy levels of all radiation in the electromagnetic spectrum. Gamma rays are emitted from the nucleus of radioactive substances as a result of transitions of protons and neutrons between two energy levels of the nucleus. X-rays, on the other hand, are the result of the de-excitation of electrons to a lower energy state. The energy of gamma rays ranges between 10 thousand electron volts (KeV) and 10 million electron volts (MeV).

The mechanism of gamma ray interaction with matter is a complex function of the radiation energy and the atomic number of the material (Kircher, 1964). At low energies, the gamma photon is completely absorbed by an electron and the electron is ejected from the atom (photoelectric effect). At higher energies, the photon can eject more strongly bound electrons, with the photon being scattered at a reduced energy (Compton effect). The scattered photon can also interact with electrons. At still higher energies, the gamma ray can interact with a nucleus and be absorbed, resulting in the production of two particles, a positive and a negative electron (pair production). The minimum photon energy for pair production is 1.02 MeV.

In each of the mechanisms described above, energetic electrons are produced, and it is this internal electron bombardment that actually causes chemical changes in a material irradiated by gamma rays. Rupture of chemical bonds results from the electron bombardment; thus organic hydrocarbons can be effectively degraded by gamma radiation.

Commercial sources of gamma radiation generally are unstable isotopes of cesium and cobalt. Gamma rays from cesium and cobalt-60 sources have energies in the range of 0.40 to 1.33 MeV. In this range, the primary mechanism of gamma ray interaction with matter is the Compton effect.

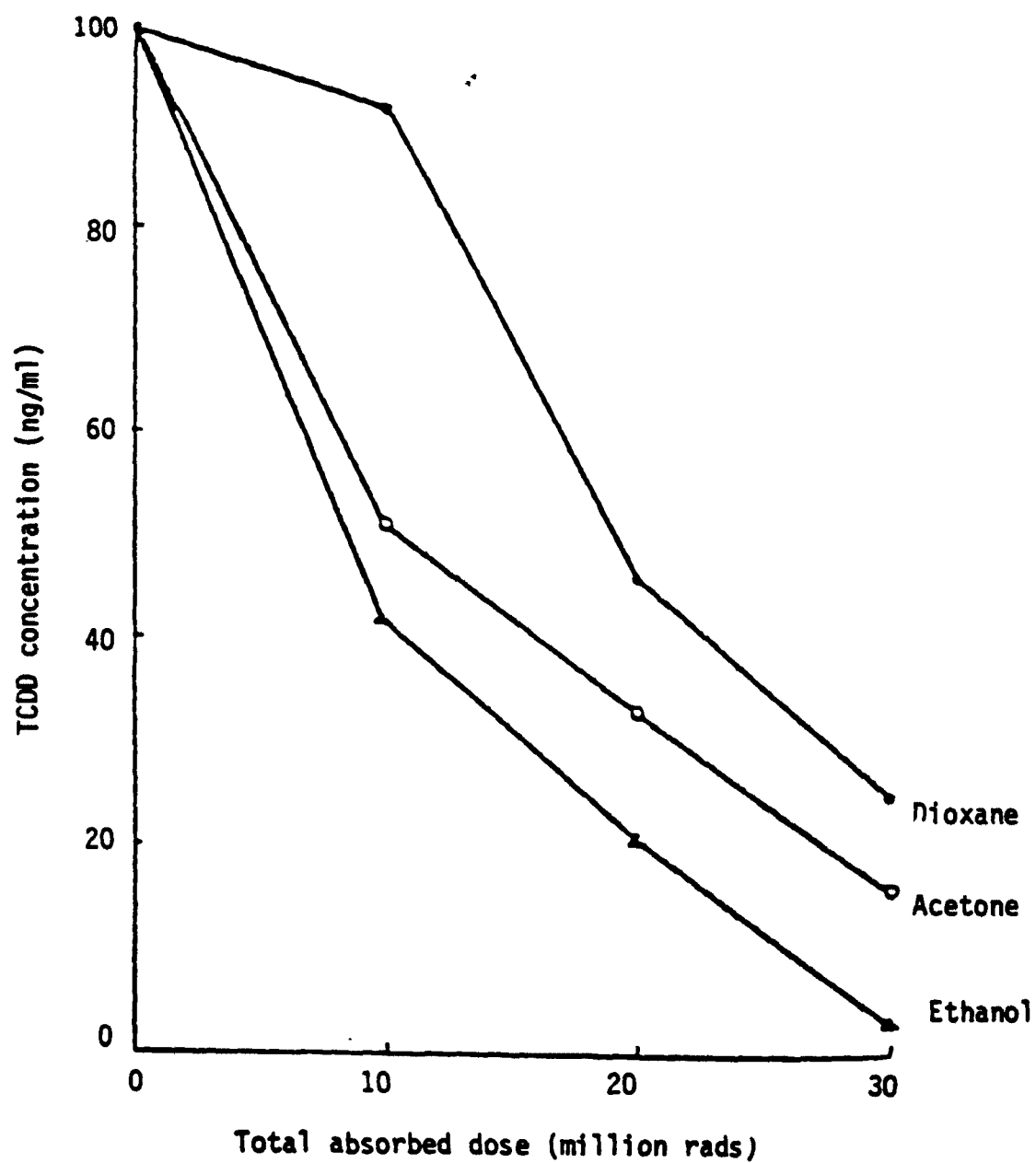


Figure 5.8.1. Effect of Gamma Ray irradiation on 2,3,7,8-TCDD concentration in ethanol, acetone and dioxane [Fanelli, 1978].

Further research is needed to verify the possible application of gamma ray radiolysis in the destruction of dioxin molecules in soils. Based on experimental data, it appears that a minimum dosage of 30 million rad of radiation is required to reduce the 2,3,7,8-TCDD level from 100 ppb to 30 ppb. (Fanelli, 1978).

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SECTION 6

FACTORS AFFECTING TECHNOLOGY SELECTION

Section 3 contained information on the quantities and types of dioxin wastes generated by industrial processes and residuals identified as sources of dioxin-containing waste. Table 6.1 summarizes information on their sources, their usual physical form, and estimates of present and future quantities of wastes generated within each EPA waste code. Sections 4 and 5 contained information on the technical aspects of a number of potential treatment technologies for these wastes. This information is summarized in Table 6.2.

The purpose of this section is to review this previously developed information and identify factors which would affect the selection/use of a particular technology for treating a specific waste type. This document has been concerned largely with the assessment of the technical factors relating to treatment technology performance. However, both technical performance and cost will generally be considered when selecting the most appropriate process for a specific waste stream. Both are considered in the following discussions.

6.1 TECHNICAL REQUIREMENTS FOR PROCESS SELECTION

Key factors which should be considered in assessing the technical applicability of treatment technologies to specific waste streams include:

1. Has the technology demonstrated that it can achieve 99.9999 percent DRE on CDD (or similar compounds)?

TABLE 6.2. SUMMARY OF TREATMENT PROCESSES

Process name	Applicable waste streams	Stage of development	Performance/ destruction achieved	Cost	Residuals generated
Stationary Rotary Kiln Incineration	Solids, liquids, sludges	Several approved and commercially available units for PCBs; not yet used for dioxins	Greater than six times DRE for PCBs; greater than five times DRE demonstrated on dioxin at combustion research facility	\$0.25 - \$0.70/lb for PCB solids	Treated waste material (ash), scrubber wastewater, particulate from air filters, gaseous products of combustion
Mobile Rotary Kiln Incineration	Solids, liquids, sludges	EPA mobile unit is permitted to treat dioxin wastes; EMSCO unit has been demonstrated on PCB waste	Greater than six times DRE for dioxin by EPA unit; process residuals delisted	NA*	Same as above.
Liquid Injection Incineration	Liquids or sludges with viscosity less than 10,000 cP (i.e., pumpable)	Full scale land-based units permitted for PCBs; only ocean incinerators have handled dioxin wastes	Greater than six times DRE on PCB wastes; ocean incinerators only demonstrated three times DRE on dioxin containing herbicide orange	\$200 - \$500/con	Same as above, but ash is usually minor because solid feeds are not treated
Fluidized-bed Incineration (Circulating Bed Combustor)	Solids, sludges	CA Technologies mobile circulating bed combustor has a TSCA permit to burn PCBs anywhere in the nation; not tested yet on dioxin	Greater than six times DRE demonstrated by CA unit on PCBs	\$60 - \$120/con for CA unit	Treated waste (ash), particulates from air filters
High Temperature Fluid Wall (Huber AER)	Primarily for granular contaminated soils, but may also handle liquids	Huber stationary unit is permitted to do research on dioxin wastes; pilot scale mobile reactor has been tested at several locations on dioxin contaminated soils	Pilot scale mobile unit demonstrated greater than five times DRE on TCDD - contaminated soil at Times Beach (79 ppb reduced to below detection)	\$300 - \$600/con	Treated waste solids (converted to glass beads), particulates from baghouse, gaseous effluent (primarily nitrogen)
Infrared Incinerator Contaminated soils/sludges (Shirco)	Pilot scale, portable unit tested on waste containing dioxin; full scale units have been used in other applications; not yet permitted for TCDD	Greater than six times DRE on TCDD-contaminated soil	Treatment costs are \$200 - \$1,200 per ton	Treated material (ash); particulates captured by scrubber (separated from scrubber water)	

TABLE 6.2 (continued)

Process name	Applicable waste streams	Stage of development	Performance/ destruction achieved	Cost	Residuals generated
UV Photolysis	Liquids, still bottoms, and soils can be treated if dioxin is first extracted or desorbed into liquid	Full scale solvent extraction/UV process was used to treat 4,300 gallons of still bottoms in 1980; thermal desorption/UV process currently undergoing second field test	Greater than 98.7% reduction of TCDD using solvent extraction/UV process - residuals contained ppm concentrations of TCDD; thermal desorption/UV process demonstrated reduction of TCDD in soil to below 1 ppb	Cost of treating the 4,300 gallons of still bottoms using solvent extraction/UV was \$1 million; thermal desorption/UV estimated to cost \$250 - \$1,250/ton	Solvent extraction/UV process generated treated still bottoms, a solvent extract stream, and an aqueous salt stream; thermal desorption/UV generates a treated soil stream and a solvent extract stream
Chemical Dechlorination-APEG processes	Contaminated soil (other variations of the process used to treat PCB-contaminated oils)	Slurry process currently being field tested at pilot scale; in situ process has been tested in the field	Laboratory research has demonstrated reduction of 2,000 ppb TCDD to below 1 ppb for slurry (batch process); laboratory and field testing of in situ process not as promising	\$296/ton for in situ APEG process; \$91/ton for slurry (batch) process	Treated soil containing chloride salts (reagent is recovered in the slurry process)
Biological Degradation-primarily in situ addition of microbes	Research has been directed toward in situ treatment of contaminated soils - liquids are also possible	Currently laboratory scale-field testing in next year or two	50-60% metabolism of 2,3,7,8-TCDD in a week long period under lab conditions using white rot fungus - reduction to below 1 ppb not achieved	NA	Treated waste medium such as soil or water with TCDD metabolites depending on microorganisms
Chemical Degradation using Ruthenium Tetroxide	Liquid or soil wastes - possible most effective in decontaminating furniture, other surfaces	Laboratory scale - no work reported since 1983	Reduction of 70 ppb TCDD to below 10 ppb in 1 hr (on soil sample)	NA	Treated medium plus the solvent which has been added (water, CCl ₄); TCDD end products not known
Chemical Degradation using Chloroiodides	Liquid or soil - thought to be most applicable to decontaminating furniture and buildings	Laboratory scale - no work reported since 1983	Up to 92% degradation on solution of TCDD in benzene - reductions to below 1 ppb were not demonstrated	NA	Treated waste medium; degradation end products are chlorophenols
Gamma Ray Radiolysis	Liquid waste streams (has been applied to sewage sludge disinfection)	Laboratory research; no research currently being conducted	97% destruction of 2,3,7,8-TCDD in ethanol after 30 hours - 100 ppb to 3 ppb	Cost for sewage disinfection facility treating 4 tons per day is \$40 per ton; TCDD treatment would be more expensive	Less chlorinated dioxin molecules are the degradation end products in addition to the treated waste medium

TABLE 6.3. TREATMENT TECHNOLOGY SELECTION CHART

Process	Has demon- strated six nines DRE on dioxin and/or reduction of dioxin in residuals to below 1 ppb	Has demon- strated six nines DRE of PCBs	Mobile or transportable process can be constructed	Process can be carried out in situ (without excavation of soil)	Can treat solids such as soils and heavy sludges	Can treat liquids and low viscosity sludges	Currently being investigated with regard to dioxin waste	Is a pre- treatment or temporary process	Is a final process
Stationary rotary kiln		X			X ^b	X	X		X
Mobile rotary kiln	X ^a	X	X		X ^b	X	X		X
Liquid injection incinerator		X				X			X
Fluidized bed (circulating bed combustor)		X	X		X ^b	X			X
High temperature fluid wall (Haber AER)	X ^b	X	X		X ^b	X	X		X
Infrared incinerator (Shirco)	X		X		X		X		X
Plasma arc		X	X			X	X		X
Molten salt		X	X ^a		X ^b	X			X
Supercritical water	X ^c		X		X ⁱ	X ^b	X		X
In situ vitrification				X	X				X
Solvent extraction					X ^b	X	X	X	
Stabilization/fixation				X	X		X	X	
UV photolysis	X ^c				X ⁱ	X	X		X
Chemical dechlorination (APEC)	X ^d		X	X ^f	X ^b	X	X		X
Biodegradation				X	X ^b	X	X		X
Ruthenium tetroxide					X ^b	X			X
Chloroiodides					X	X ^b			X
Gamma ray radiolysis						X ^b			X

^aEPA mobile rotary kiln.^bTheir stationary unit is permitted to do research on dioxin wastes.^cDeveloper has indicated this, but presented no data.^dUsing laboratory scale equipment.^eOne developer is designing a mobile unit.^fThere exists both an in situ and a batch reactor process.^gHigh ash wastes may pose problems.^hIndicates primary waste type.ⁱSolids only treated if some sort of extraction/desorption process removes the dioxin from soil.

6.1.3 Mobile/Transportable Technology

The ability to bring the waste treatment unit to the waste site is very important, particularly when treating "dioxin" waste. The transportation of dioxin waste is very controversial, and has been opposed by the public in several instances. For example, an attempt was made to obtain permission to transport dioxin-containing leachate to the SCA incinerator in Chicago. Illinois residents strongly objected to this, and local authorities indicated that drastic measures would be used to block the effort (Gianti, 1986). As a result, many of the developing thermal and nonthermal technologies are being designed to function as mobile/transportable units that can be taken to the waste site. The units that are mobile are identified in Table 6.3. Stationary treatment facilities, even though they are able to demonstrate high levels of destruction, may not be fully utilized for highly toxic dioxin wastes.

In addition to avoiding the risk of spillage during transportation, another advantage of the use of a mobile unit is that the cost of transporting the waste to the treatment facility is eliminated. For each of these reasons, processes that are designed to be mobile appear to be more useful for treating listed dioxin wastes.

6.1.4 In Situ Technology

Similarly, processes that can treat the waste in situ may also be advantageous. In situ processes are aimed primarily at contaminated soil. Most processes require that the soil be excavated and then be fed to the treatment process. A process in which the excavation step is eliminated may be more environmentally and economically acceptable than a process that relies on excavation of the waste. Not only is excavation expensive, but it may also result in the dispersal of contaminated soil particles and greater human exposure to the contaminant. Processes with the potential for in situ use include chemical dechlorination, in situ vitrification, biodegradation, and stabilization/fixation. Chemical dechlorination, using potassium polyethylene glycol (KPEG), has been tested both as an in situ and a batch reactor type of process. As indicated in Section 5, the batch reactor variation of the

gamma ray radiolysis. Other technologies, including both fluidized bed and rotary kiln incineration, chemical dechlorination, and the high temperature fluid wall process have been used to treat both liquid and solid wastes. Finally, other processes are designed to be used primarily for either liquids or solids, but if certain pretreatment measures are applied, they may be able to treat both waste forms. For example, ultraviolet (UV) photolysis is only effective in treating waste streams that the radiation can penetrate, such as a nonabsorbing liquid. If, however, the contaminant is first desorbed, either thermally or using an organic solvent, a contaminated soil waste can be treated using this technology.

Perhaps the most important factor with regard to the physical properties of a waste stream is that each waste stream must be treated individually, and variations in waste characteristics fully assessed, to ensure that unanticipated difficulties do not arise. Even though pilot or laboratory scale data may indicate that a certain waste form is easily treatable, processing of the actual waste stream may pose problems. One example of this is the trial burns of Vertac still bottoms at the Combustion Research facility. The waste stream, on the basis of preliminary evaluations, was originally pumped through a feed lance into the rotary kiln without dilution or mixing with fuel. However, the lance frequently became inoperative due to clogging and carbon buildup, and the waste feed had to be interrupted so the lance could be cleaned. The problem was finally rectified by diluting the waste with water prior to pumping it into the kiln (Ross et al., 1986). Another example is the application of KPEGs directly to soil (in situ) to dechlorinate TCDD. In the lab, the process was fairly successful, but when applied in the field the KPEG reagent was seriously degraded by moisture in the soil, and the resulting degradation of TCDD was minimal. A third example involves the Huber AER. This unit was originally tested on very granular, uniform materials such as sand. In reality, all contaminated solids or soils are not as dry and uniformly graded as sand. Consequently, when the Huber reactor was tested on actual waste, there were problems with the feed mechanism. Special pretreatment measures to produce a granular, free-flowing feed had to be incorporated (Boyd et al., 1986).

To summarize, waste characteristics and process capabilities must be carefully evaluated before the appropriate treatment technology can be applied.

The cost of treating dioxin-containing waste is very much affected by the high level of risk associated with the treatment of these waste streams and their residuals. Generally, processing of these wastes requires the imposition of extraordinary and often redundant measures to ensure that risks are not incurred by workers and the general population. One example of this was the attempted incineration several years ago of 6,000 gallons of solvent waste contaminated with 14 ppb of TCDD. The Dioxin Disposal Advisory Group (DDAG) recommended incineration of the waste at the ENSCO incinerator in Arkansas. ENSCO usually charges \$325 per 55-gallon drum of hazardous waste, but in this case they would have charged \$45,000 for the waste plus a \$150,000 surcharge because it contained dioxin (Technical Resources, Inc. 1985). This amounts to a unit cost of approximately \$30/gallon (\$1,500 per 55-gallon drum) or \$6,000/ton for 10 lb/gallon waste. In the end, however, ENSCO refused to accept the waste because of overwhelming public opposition (and implied liability).

Cost will always be an important factor in the selection of a treatment method, but at this time the demonstration of technical and environmental effectiveness appears to a more overriding concern. Technology must be fully demonstrated for treating dioxin wastes if public concerns are to be addressed and reconciled with the need for effective treatment.

6.3 SUMMARY

Each of the technical and cost factors discussed above will affect the final selection of a technology to treat the waste. It is important to keep in mind that the field of dioxin waste treatment is in a developmental stage. At the present time, only a few of the technologies have demonstrated 6 nines DRE on CDDs and CDFs, although many of the technologies are now undergoing performance testing using dioxin waste, or will undergo testing in the near future. In addition, with the ban on land disposal of dioxin wastes scheduled to go into effect in November 1986, work on the development of additional new technologies for treating these wastes can be expected to accelerate. Information in this document represents the developmental status of dioxin waste treatment technologies in the spring of 1986; revisions will be required as anticipated technical advances are made in the future.